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PHYSICO-CHEMICAL GEOLOGY

BY

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NEW YORK
LONGMANS, GREEN & CO.
LONDON: EDWARD ARNOLD & CO.
1927

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PREFACE

This book is an attempt to give in a connected form some account of the application of modern theories of physical chemistry to geological problems. It is not intended for beginners in geology, since an acquaintance with the general principles of the science, as set forth in any elementary textbook, as well as some knowledge of mineralogy, is assumed.

It is fully recognized as being incomplete, but this is almost a necessity of the case, if the book is to be kept within any reasonable compass. The scope of the subject is so enormous, that it would have been possible to go on to an almost indefinite extent, but it is hoped that the line of treatment of certain elementary problems here adopted may be found of value in paving the way for the more precise study of some branches of geology which have hitherto suffered from a certain want of precision in their statement, with an inevitable and consequent vagueness in the conclusions drawn from the available data. Of late years much information of high scientific value has been obtained from researches actually, though not always explicitly, carried out from an economic motive. Great use has been made of these, as well as of the vast mass of geological and mineralogical literature now existing. To enumerate even the most important sources of information would expand this preface to inordinate length, and it is believed that in all cases due acknowledgment has been made in the text or in footnotes.

I am indebted to Dr. N. L. Bowen for permission to copy several of his figures, which in some cases have been slightly modified to accord with his later results.

All the figures, with one exception, have been drawn for me by Mr. A. N. Lanham, of the Department of Mineralogy, Cambridge University, to whom I am greatly indebted for the skill and care devoted to their production.

R. H. R.

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PHYSICO-CHEMICAL GEOLOGY

CHAPTER I

THE STATES OF MATTER AND THE PRINCIPLE OF EQUILIBRIUM IN GEOLOGY

Introduction. It is unnecessary for the special purpose of this book to enter into a discussion of the ultimate constitution of what we may still as a matter of convenience continue to call matter: the higher flights of molecular and atomic physics have hardly as yet entered into the sphere of the applied sciences, such as geology and mineralogy. We may still without hesitation speak of atoms and molecules and the other fundamental ideas of the chemistry and physics of the last few decades. If the terminology here employed may perchance seem a little old-fashioned to the modern physical chemist, and more especially to the physicist, no apology is here offered. The writer's chief object has been to use language that will be readily understood by all students of elementary science. Furthermore the mathematical treatment of the subject has been reduced to a minimum.

The geologist, whether his chief interest lies in the pure science or in the practical applications of it, is concerned with matter in its various forms, and with energy: it is with the effect of varying forms of energy on matter that he mainly has to deal. The basis of the greater part of modern physical chemistry is the idea of equilibrium: the special feature of physico-chemical geology is that the conditions of equilibrium are constantly undergoing variation, owing to the operation of external natural causes. Hence the subject is in reality a very complicated one. Processes do not go on as smoothly in nature as they do in a laboratory; there is a constant outside interference to be taken into account. Nevertheless the conditions of equilibrium proper to natural processes can be and have been determined in a great number of cases, throwing a flood of light on their actual working, and on the origin of many substances of technical value, as well as pointing out the way towards a more rational and economic utilization of natural products, and leading to more scientific and organized methods of search for further deposits of similar or cognate nature. Of late years a great amount of research has been conducted on the physics and chemistry of minerals, having as its real object a commercial application, although this real object is not always apparent in the publication of the results.

The States of Matter. The geologist and the mineralogist in the course of their ordinary work have to deal to a large extent with the transformations of matter from one state of aggregation to another, as exemplified by the freezing of water, the deposition of salts from solution, the weathering of rocks by oxidation and other chemical processes, crystallization from igneous magmas and the formation of minerals from fluids at all grades of temperature and pressure. All these processes involve a change of state in the whole or a part of the material concerned, usually from solid to liquid or vice versa, less commonly a direct passage between the solid and the gaseous states. There are also many examples of changes from one solid form to another without alteration of chemical composition. Further there is that great class of phenomena which may be summed up in the general term of chemical reactions, all of these being controlled by physical laws of character analogous to those governing changes of state.

Thus we arrive at the popular conception of the three states of matter: solid, liquid and gaseous; a conception useful in itself and containing much truth, but difficult to apply strictly and in a scientific manner. The chief obstacle lies in the absence of sharp boundary lines between the three states in certain special cases, even in common substances. In the case of water under atmospheric pressure the difference is sharp and clean: ice, water and steam are each clearly marked off from the others, with no intermediate forms, each pair having its own appropriate transition temperature, ice melts to water at 0° C. and water boils to steam at 100° C. But the common practice of superheating steam in a boiler shows that the boiling point is not really fixed, but varies with the pressure. If this process is carried far enough a point is eventually reached at which the distinction between water and steam disappears. This is called the critical point for water, and lies at 375° C. and about 200 atmospheres pressure. Above this point the substance H_2O can exist in only one form, which cannot properly be described as either a liquid or a vapour; the term fluid is, however, still applicable. If water is present as such in the earth's interior below a certain depth it must be in this condition.

Again, if we warm a jelly in a pan or heat a piece of glass in a gas flame, they will soften and pass gradually by decrease of viscosity into a liquid form. In this case there is no sharp change of condition, as in the melting of ice. Here we have a fundamental conception in the study of the states of matter, the idea of continuous as opposed to discontinuous changes. In the case of glass and jelly it is impossible to fix any precise point at which they can be said to melt, whereas in the case of ice the melting is not only quite sharp and definite, but there is also a sudden change of volume. As will be discussed in detail later all such discontinuous changes involve abrupt alteration in the thermal state of the system, that is in the amount of energy that it contains. Such is not the case with continuous changes like the softening of glass, or the melting of jelly, where there is no physical break of any kind and therefore no definite heat-effect or energy-change. This fact at once leads to the conclusion that there are in fact two kinds of solids, with different characteristics and essentially different modes of formation. As will be seen later, hardness is no true criterion of physical constitution. It is the nature of the molecular structure that really matters, and this is intimately bound up with the mode of formation.

Even a very slight acquaintance with geological processes is sufficient to show that natural substances vary very widely in their degree of permanence under various conditions. (Some minerals appear to be almost indestructible, at any rate by natural processes, while others undergo alteration with the greatest ease. Some minerals are permanent under almost all conditions, while others, though really or apparently stable under one set of conditions, easily undergo alteration when these conditions are changed. This last-named category is easily observed in the processes of metamorphism, and is in fact also the foundation of the chemical processes of weathering and of many other changes occurring in rocks.) As a matter of fact geological processes consist largely of adaptation to environment, using this expression in a physico-chemical instead of a biological sense. The fundamental basis of natural processes is in reality one of adaptation to changing conditions, or to use the word now commonly employed, a tendency towards the establishment of equilibrium as conditioned by external factors.

Equilibrium. Since the idea of equilibrium is the foundation of so large a part of the modern treatment of physico-chemical problems, it is essential to have a clear idea of what is meant by this term. Stated in popular language a mass of matter in any state or states of aggregation is in equilibrium when it is existing under such external and internal conditions that there is no tendency to change of any kind. Such a mass can exist indefinitely *in statu quo* provided that no alteration takes place in the external conditions. Thus a quantity of water or any other liquid tightly corked up in a completely full bottle is in equilibrium under the ordinary conditions of temperature and pressure. There is only one substance present, water, and it does not change into any other substance or form, within certain limits, e.g. between its freezing and boiling points. It is of course also implied that there is no chemical action between the liquid and the walls of the vessel. Inside the bottle only one substance exists and its properties are uniform in every part. It is therefore said to be in homogeneous equilibrium. The same is also true of all unsaturated solutions and of gases, either simple or mixed, in closed vessels.

On the other hand water standing in an open bucket is not in equilibrium with the atmosphere, unless the atmosphere is completely saturated with water vapour. Otherwise there will be evaporation ; the liquid water changes into a gas, and there is no equilibrium. No substance which is in the least degree volatile can be stable in an open vessel, except under exceptional conditions.

In the conception of homogeneous equilibrium it is implied that every part of the mass in question has exactly the same chemical and physical characters. As a matter of fact this state of affairs is not prevalent in nature, and this type of equilibrium is not of much importance.

It is with the second type, or heterogeneous equilibrium, that we are mainly concerned. In so far as equilibrium exists at all in geological processes it belongs mainly to this second category, in which a system composed of matter in two or more chemical and physical conditions is in a stable state. It may indeed be said truly that the great majority of natural processes may be regarded as a striving after heterogeneous equilibrium which is never attained, owing to continual variations in external conditions. The processes of nature do not work so smoothly as those which can be carried out in a laboratory, and even with the best of means real uniformity and constancy of conditions can rarely or never be attained even artificially, though very close approximations can be made in experimental work. However, the study of artificial equilibria and the rules governing them has thrown a flood of light on natural phenomena, on the processes of geology, the weathering, alteration, and decomposition of rocks, the origin of rocks and minerals and all the other innumerable transformations going on in the crust of the earth.

As before stated, then, it is possible for equilibrium to exist in a system, the parts of which differ in physical properties and often also in chemical composition and are separated from one another by definite surfaces of discontinuity. Thus under a certain range of physical conditions it is possible for ice and water to exist together indefinitely. Here the ice and the water have the same chemical composition but differ widely in physical properties, one being a liquid and the other a solid. The same is true of a saturated solution of a salt in contact with solid salt. Again as is well known many solids undergo changes of properties at a definite temperature and pressure, though still remaining solid, and at the transition point it is possible for both forms to exist together. Again very many solids at a certain fixed point melt to a liquid, and liquids boil, and at all temperatures most liquids undergo more or less evaporation. When a liquid is evaporated in a closed exhausted vessel, evaporation or boiling continues till the pressure of the vapour reaches a certain point. Further, as will be seen later, at one fixed point of temperature and pressure, and at one point only, can ice, water and water-vapour all exist together. This is an example of the equilibrium of three different substances, which, however, in this case have the same chemical composition. In the same way there may be a stable system of ice, salt, salt-solution, and water-vapour only at one fixed point. Here there are two different substances, water and salt, in four forms. From these examples it is obvious that there is some connection between the number of substances present and the degree of variability of conditions consistent with the maintenance of equilibrium. The laws governing these phenomena were first worked out theoretically on thermodynamic grounds by Willard Gibbs, and are embodied in the great generalization now universally known as the *Phase Rule*. Since this law is in reality the foundation of the greater part of our theoretical discussions, it will have to be considered later in detail.

In considering the nature of equilibrium between two masses of dissimilar matter, e.g. liquid and solid, or liquid and gas, it is necessary to look at it also from the kinetic point of view. All matter is to be regarded as consisting of particles or centres of energy in a state of motion: the molecules of gases are in most active movement, those of liquids less so, those of solids still less, but still possessing movement and therefore energy. The free energy of a solid cannot be measured directly, but expresses itself for example in heat changes on crystallization or melting; similarly with evaporation and condensation in liquids and gases. Now when a liquid and a solid, for example a soluble salt and water, are in contact, they will be in equilibrium when the amount of salt dissolved in a given time is exactly equal to the amount solidifying (crystallizing) from the solution in the same time. When a gas and a liquid are in equilibrium also, or a gas and a solid, the number of molecules passing in either direction across the bounding surface are equal. Similarly we may speak of a complex chemical system as being in equilibrium when all the possible compounds that can be contained in it are being formed and decomposed at the same rate. Hence it is seen that there is no real distinction between a purely physical equilibrium such as that between ice and water and the chemical equilibrium between two salt-pairs in solution in what is commonly called a double decomposition. Or there may be only one term on one side of the equation, as in the well-known instance of the decomposition of calcium carbonate by heat.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

Such a process is often called dissociation, since one compound breaks up into two which are clearly separate physical entities. This dissociation however soon stops, or in other words, a state of equilibrium is soon attained, unless one of the products is removed. This is in reality quite analogous to the evaporation of water in a vacuum, as before mentioned. In either case, so soon as the gas pressure reaches a certain point, determined by the temperature, the reverse process sets in, water or calcium carbonate are again formed as fast as they are vaporized or dissociated and equilibrium is reached. This general principle, and especially the particular case of the dissociation of limestone, is of special importance in the study of metamorphism. In the nature of things it is in processes going on far underground, where conditions change most slowly, that we are likely to find an approximation to the establishment of a truly stable state of matter over long periods of time.

Thus according to the point of view adopted, equilibrium may be regarded as static, a stable state of no observable change, or kinetic, where two or more equal and reversible processes are in constant operation, but are constantly neutralizing each other, and leading to a condition of balanced action. Both conceptions are equally true and equally useful. From either point of view it is clear that when a system is in a state of stable equilibrium, its component and discrete parts must possess equal energy: if it were not so, if one part had more energy than the other, further changes must set in. Hence we may say that in any system in equilibrium the free energy must be at a minimum.

It is important to remember that in heterogeneous systems the equilibrium is independent of the absolute amounts of the substances present. Thus in the common case of a saturated salt solution, the composition of the solution is the same (under constant temperature and pressure) whether it is in contact with an ounce or a pound or a ton of solid salt.[1] But suppose now that more and more water is added to the same solution at the same temperature : the concentration of the solution will remain the same till all the salt has been dissolved. When this happens however the system is no longer heterogeneous, but homogeneous, and any further addition of water will make the solution more and more dilute. This well illustrates the fundamental difference between heterogeneous and homogeneous equilibrium, and also the close connection between them, since a system can pass from one to the other by mere addition or subtraction of constituents.

It also illustrates another point of great importance, namely, that the term equilibrium when applied to the relation of *two* or more substances should only be used when *both* or all the substances are actually present in their proper forms, e.g. a saturated salt solution can only be said to be really in equilibrium with the salt when the latter is actually present in the solid form. Unless the solid is there too it is practically impossible to determine that the solution is saturated. And this leads on to a short and preliminary consideration of what are called false equilibria.

False and Unstable Equilibria. This subject cannot be gone into fully here, as it is of the very greatest practical importance, and will recur again and again in later sections. The significance of the expression can be well illustrated in a general way by the very common phenomenon of supersaturation. When a nearly saturated hot salt solution is cooled down carefully without disturbance and in the absence of any of the solid salt, it is often found that the salt does not necessarily begin to separate as soon as the true saturation point is reached : the solution can in point of fact often be cooled down far below this point : it is said to be supersaturated. But if a crystal of the salt is then dropped in solidification of the salt will begin at once. In the same way a fused substance may be cooled down below its true freezing-point ; crystals may refuse to separate from a melt and solid transformations may be long delayed, or may fail to occur at all. All these supersaturated or under-cooled systems are said to be in a state of unstable equilibrium. It is now customary to recognize two types of this : metastable equilibrium, when the change of state can only be brought about by the introduction of the substance that ought to be formed (inoculation) and labile equilibrium when the change can take place spontaneously after a time. This distinction does not seem to be of much real importance. What does matter is that such delayed changes are extraordinarily common in natural processes and have led to very great difficulties in their interpretation by physico-chemical laws. They also offer a great bar to successful experimental work along many important lines of research. It is clear that in many transformations the attainment of true equilibrium is a very slow process, sometimes almost infinitely slow, as shown by the existence together in nature of two or more forms of the same thing, with different physical properties, which cannot all be really stable. As a broad generalization it may be said that equilibrium is as a rule the more quickly attained the higher the temperature is, up to the transition point. This applies more particularly to transformations in the solid state, and it is in effect the basis of the innumerable varieties of heat-treatment now applied to steel and other metals. The converse to it is quenching, where the metal or other substance is cooled down as quickly as possible far below the transition point, so that there is no time for equilibrium to establish itself. By this means it is possible to preserve compounds and structures which are really only stable at high temperatures, and to investigate them, microscopically or otherwise, at leisure. The experimental side of geology and mineralogy has already learnt much, and is likely to learn much more, from the comparatively new science of metallography: the alloys show much analogy to minerals and rocks, both in their structures and in their thermodynamic relations, and some natural alloys actually exist as minerals.

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[1] This statement is not quite true when the absolute amount of solution is very small, as then surface effects become prominent, owing to the high ratio of surface to total volume.

Supersaturation. It will be convenient to consider here in a little more detail what actually happens in the case of undercooling of melts or supersaturation of solutions. This subject, which is of immense importance in the study of natural and artificial geological and mineralogical processes, has been carefully investigated by Tammann, who established a general principle as follows: the tendency towards the formation of a solid phase, or velocity of crystallization, in a supersaturated liquid, in the original absence of the solid, increases as the temperature falls below the true freezing-point up to a certain maximum value and then again decreases on further fall of temperature. Hence it follows that if a melt or solution is cooled rapidly through the critical range crystallization will be in effect inhibited altogether; such unstable equilibria far below this range become in practice very stable. At the same time the viscosity of the liquid increases very greatly. Thus, for example, a silicate melt always very viscous even above its freezing-point, under these conditions will pass gradually into a substance having in a marked degree the properties of a solid, especially hardness and brittleness. Such a substance is called a *glass*, and is not in reality a true solid, but an undercooled liquid. It is important to remember that the term velocity of crystallization as used above in connection with the starting of crystal-formation is not the same thing as the rate of increase in size of crystals after growth has begun. One process consists in the formation of crystalline nuclei, the other in the addition of material to surfaces already in existence. No doubt surface tension plays an important part in both these processes, but is much more important in the former case, owing to the small size of the nuclei and the consequent high ratio of surface to volume.

Thermal Effects. Since changes of state, such as freezing, melting, solution or transformation from one solid form to another are accompanied by some thermal effect, either evolution or absorption of heat (exothermic or endothermic effects) it is obvious that this factor has also to be taken into account in any consideration of equilibrium, and in point of fact a chemical equation indicating a change of this sort is incomplete unless the thermal effect measured in units of heat either absorbed or liberated, is also indicated.

When a system hitherto in equilibrium under a given set of conditions is subjected to an alteration of those conditions, some internal change must also take place in the nature of adjustment to the new state of affairs. Thus to take a very simple case, namely, the effect of pressure on solubility: as a general rule solution of a solid in a liquid is accompanied by a diminution in the total volume of the system. Now pressure also obviously will favour compression, therefore pressure will increase solubility in this instance. If the volume of the solution is greater than the sum of the volumes of the separate constituents, the opposite effect will be produced, and the solubility of the solid is diminished by pressure. In point of fact the effect of pressure on the solubility of solids in liquids is usually very small as measured by figures obtainable experimentally but at the enormous pressures that prevail in deep-seated regions of the earth it is doubtless of importance. Again when, as is usual, freezing is accompanied by diminution of volume, it will be favoured by pressure. Molten material under high pressures will therefore freeze or crystallize at higher temperatures, or in other words the freezing point will be raised by pressure. This is a point of fundamental importance in geological physics and will recur frequently in subsequent discussions. It must suffice here to say that, given certain experimental data, the question can be reduced to a quantitative form.

It is obvious then, without going further into specific detail, that the changes of equilibrium due to variations of physical conditions must be subject to a general law. This law was set forth in general terms by Le Chatelier and later elaborated and reduced to a quantitative expression by Van't Hoff and other workers. It may be stated in the following general terms: "when a system in equilibrium is subjected to some external constraint, that change will take place which tends to counteract the effects of the external constraint." In simple language this means that increase of pressure will favour changes involving contraction of volume and an increase of temperature will favour changes accompanied by absorption of heat. This law applies in a perfectly general way to all types of change of state, both to changes from solid to liquid, liquid to vapour and solid to vapour and their respective reverse processes, and also to transformations from one form to another in the same state of aggregation, namely, the inversions from one crystalline form to another that are so common among minerals. The changes may be long delayed, but until they do take place the substances are actually in a state of unstable equilibrium.

When stated in this way this "law" is in reality only an application of cold common sense: it is fairly obvious that matter will resist external changes as much as possible; when a system is in equilibrium it is in the most stable state possible, and it will, so to speak, do its best to remain in a stable state in spite of outside interference. This is a somewhat biological or anthropomorphic way of looking at a purely physical phenomenon, but it contains much truth.

Cooling Curves. It is necessary now to consider a little more in detail the phenomena attending a change of state of aggregation of matter. It has already been mentioned that some substances when heated undergo a complete and discontinuous change, like ice or lead, whereas others, like glass or jelly, gradually soften and become more or less liquid by continuous decrease of viscosity. Hence there are evidently two kinds of solids, using the term in its popular sense. One kind passes into a liquid without any abrupt and definite change of state and properties, like glass. Let us contrast this with the behaviour of a metal. When a mass of lead is heated its volume slowly increases as the temperature rises: when a certain definite temperature, 327° C., is reached, the metal suddenly and completely melts, or passes into the liquid state, with an abrupt change (increase) of volume. The liquid on further heating continues to expand slowly and regularly, not necessarily at the same rate as the solid metal. Another important point is that there is also a definite heat-effect, the temperature remaining constant while the metal melts. The change of state can be well expressed by a diagram in which specific volume (the reciprocal of the density) is plotted against temperature. Such a curve will have the form shown in Fig. 1. The vertical portion of the curve represents the discontinuous change of state. If a similar curve is constructed for a mass of glass it is found that the volume curve dv/dt is a continuous function of the temperature, with no change of direction (Fig. 2). Further, in such a case there is no heat-effect. The presence or absence of a heat-effect in all such cases can most easily be shown by means of a heating or cooling curve, in which temperature is plotted against time. Observations of temperature taken at regular intervals are used as ordinates, the abscissæ being time intervals. In the case of changes with a definite heat effect, such will be shown by the form of the curve. In practice cooling curves are usually employed. In the case of the solidification of a crystalline substance the evolution of heat on crystallization (latent heat) will just counterbalance the loss of heat by radiation so long as any solid is being formed. Hence during the crystallization interval the temperature of the mass remains constant and the cooling curve shows a horizontal portion. This gives the true freezing point of the substance. The horizontal

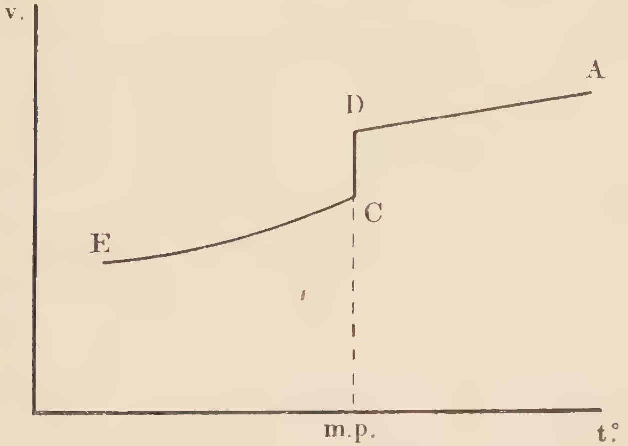

FIG. 1.—The changes of volume of a crystalline substance and the liquid resulting from its melting.

AD = volume of solid; CE = volume of liquid.

portion of the cooling curve in Fig. 3 expresses the same fact as the vertical portion of the volume curve in Fig. 1; namely, a discontinuous change of state accompanied by a thermal effect. On the other hand the cooling curve for a mass of molten glass, or of a jelly, will show no break, since there is no heat effect and no definite melting point.

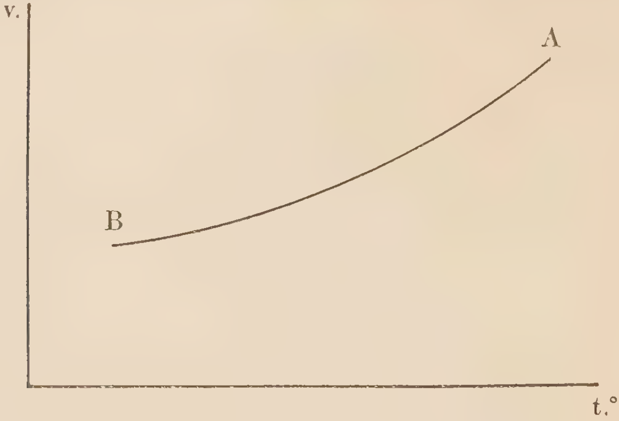

Fig. 2.—Volume curve of an amorphous substance on heating or cooling.

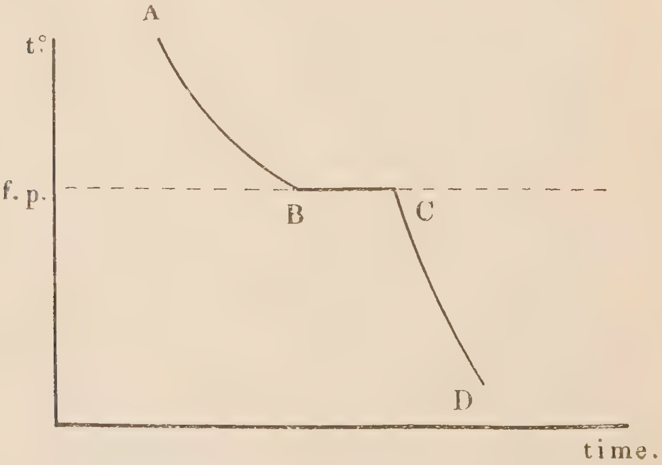

Fig. 3.—Cooling curve of a crystalline substance.

AB = cooling of liquid; *BC* = freezing; *CD* = cooling of solid. Temperature is plotted against time.

Next to be considered is a special case well exemplified by many silicate melts, both natural and artificial. The effects seen in silicate melts differ widely in many cases according to rate of cooling: that is, in fact, according to whether time is allowed for the establishment of true equilibrium. If a charge is made up in a crucible, having the composition of anorthite felspar for example, raised to a temperature well above its fusing point and then cooled quickly, it can be solidified as a homogeneous glass: the volume curve will then have the simple form shown in Fig. 2 above. If, on the other hand, the cooling is very slow, it is found that at a certain definite temperature crystals of anorthite begin to separate out, and when the whole has solidified it consists of a mass with crystalline structure. It is evident that even in this case the first part of the volume curve will be the same as before in the case of quick cooling, but at the freezing point there is a sudden contraction of volume and the rest of the curve shows the volume-changes in crystalline anorthite (Fig. 4). This figure is obviously a combination of Figs. 1 and 2; now the fused liquid to the right of the vertical portion and the crystalline mass to the left are both in stable equilibrium, hence the remaining portion of the upper curve must be in unstable equilibrium. Instead of volume, this diagram might be taken to represent the amount of free energy in the liquid or solid at the given temperatures. Then the vertical portion would represent, quantitatively, the thermal effect, namely a decrease of energy by evolution of heat (Fig. 5). Under either conception the left-hand

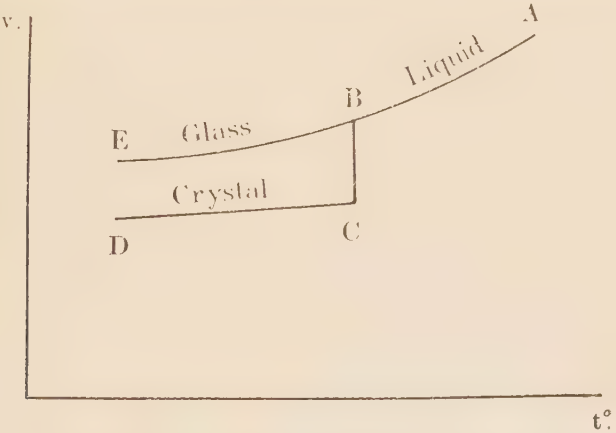

FIG. 4.—This figure is a combination of Figs. 1 and 2.

AB = liquid; *BE* = undercooled liquid; *CD* = crystalline solid.

portion of the upper curve represents the condition of an unstable substance, containing too much energy, and therefore with an innate tendency to change into the stable form. This portion may also be taken to represent a supersaturated solution, or what is the same thing, an undercooled solution. Matter in this condition is well known in nature as volcanic glasses, and its slow and gradual transformation to the stable crystalline form is called devitrification. In short it can be truly said that a glass, whether natural or artificial, is an undercooled liquid and not a true solid. All matter in this condition may be called *amorphous*, as opposed to the stable crystalline form.

It is thus seen that there is no fundamental distinction between the properties of amorphous solids and those of liquids, and it has already been shown that above the critical point liquids and gases become indistinguishable; hence all three of these, amorphous solids, liquids and gases, possess many properties in common and form one natural group, sharply distinguished from the crystalline solids. It should be briefly mentioned here that certain bodies are known which though apparently liquid, yet show double refraction: these so-called liquid crystals are only known among complex organic compounds and are therefore of no geological interest; still it is necessary to include them with the crystalline solids in a general scheme.

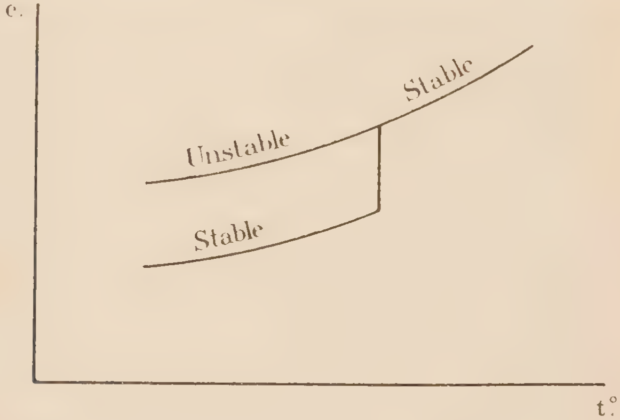

Fig. 5.—Temperature-energy curves to show stable and unstable conditions. The vertical portion represents the energy-change (heat-effect) on freezing or melting.

Summary. To recapitulate, all crystalline solids possess vectorial properties and are therefore *anisotropic*; all amorphous substances possess only scalar properties and are *isotropic*. The forms of matter can then be classified as follows.

Crystalline or Anisotropic.	**Amorphous or Isotropic.**
Crystalline solids	Amorphous solids
Liquid crystals	Liquids
	Gases

At first sight it might appear that the existence of matter in the colloidal condition is inconsistent with this scheme. It will, however, be shown later that the colloid condition is not a *class* of matter as distinct from liquids or solids, but a *state of dispersion* of at least two kinds of matter: a colloid is in fact a mixture of a solid (crystalline or amorphous) and a liquid, or a mixture of two liquids, in fact a two-phase system, and never truly homogeneous.

The foregoing classification of the different states of aggregation of matter is of fundamental importance in the physics and chemistry of geology, since this branch of science is mainly concerned with the laws governing the changes from one state to another and the nature of the products resulting from such changes. All geological processes and their results are governed by the laws of equilibrium that control such changes.

Physical Properties of Water.[1] Since water plays so important a part in geological processes in general it will be profitable to consider its properties in some detail. It must, however, be clearly understood that in many ways water is exceptional, and in some respects its behaviour under given conditions is the exact opposite of that of most other substances. This fact in itself is of great geological importance.

Within the normal range of temperature and pressure water can exist in three forms, as vapour, liquid and ice. Water vapour exists in large quantities in the atmosphere, whence it condenses as rain and snow. Liquid water is found as rivers, lakes and the sea, while where the temperature is below 0° C. it solidifies to ice. The mechanical effects of water and ice in their geological results are outside the scope of this book; it is only with the chemical and physico-chemical applications that we are here concerned. In geology and mineralogy water may be regarded as the universal solvent, and the properties of water-solutions are of first-class importance. Recent research has shown that at very low temperatures and under enormous pressures water can exist in several other solid forms. Owing to a possible geological application brief reference will be made to one of these.

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[1] In this chapter the term "water" must be taken, where required by the context, to connote the chemical compound H_2O in its various states of aggregation, solid, liquid and gaseous, and not as referring to the liquid form only.

If a given weight of water at say 20° C. is heated it will be found that its volume increases regularly up to boiling point, and if it is cooled its volume decreases down to a certain point, about 4° C. Therefore between 100° and 4° its behaviour is perfectly normal, with expansion on heating and contraction on cooling. But at 4° the sign of the coefficient of expansion changes and the volume increases again down to 0°. At this temperature the water freezes to ice with an expansion of about 10 per cent. On further cooling the volume of the ice contracts in the way common to most solids. These changes are expressed in the *tv* diagram (Fig. 6). The difference in form between the curve and that representing the behaviour of a normal substance (Fig. 1) is obvious at a glance. In both these cases the effect of pressure in displacing the curves and transition points has been ignored and atmospheric pressure is assumed throughout. The effect of pressure on freezing points will be considered later. At atmospheric pressure the normal form of ice, known as Ice I, is stable down to the lowest temperatures yet attained.

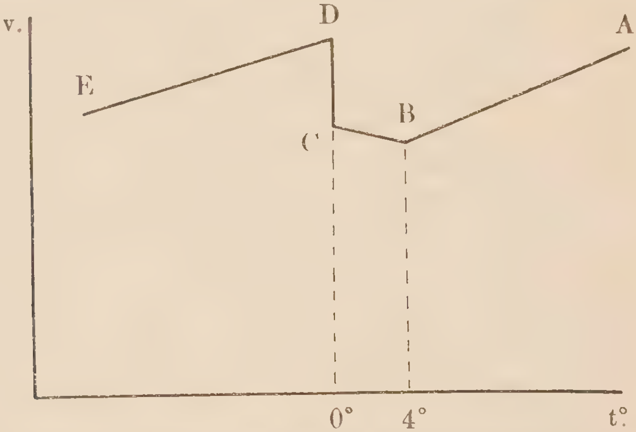

Fig. 6.—Volume curve for water passing through the point of maximum density *B* and the freezing point (diagrammatic). The volume of the solid (ice) is greater than that of the liquid.

The simple facts that the maximum density of water is at some degrees above the freezing point and that ice is lighter than water are of the utmost importance in the economy of nature, especially so, curiously enough, from the biological point of view : in fact it is hardly too much to say that were it otherwise life as we know it would be impossible over at any rate a large part of the earth. When a large body of fresh water, such as a moderate-sized lake, in a cold-temperate or cold climate cools down on the approach of water, the surface water on reaching 4° begins to sink, bringing lighter and therefore warmer water to the top by convection. This process goes on till the whole reaches 4°. Then and only then can the upper layers cool down further. The colder surface layer below 4° being now lighter than the water below remains at the top and freezes to ice, which furthermore being lighter than any of the water remains floating. Hence it is impossible for a lake to freeze to more than a moderate depth, since ice and water are very poor conductors and there can be no sinking of colder water or ice to cool the bottom layers. Now if water were at its maximum density at 0°, water at that temperature would sink and freezing would begin at the bottom, the lake eventually becoming, in a cold climate, a solid mass of ice, thus effectually destroying most forms of life. This chilling effect would of course be accentuated by the sinking of ice heavier than water.

Another point of much importance in physical geology is that if ice possessed a smaller specific volume than water there would be no shattering effect on rocks due to water freezing in cracks and pores of the rock. Thus a very significant geological agency would be non-existent, and denudation in temperate and cold climates would be very different. It is well known that the expansion of water on freezing sets up tremendous pressure in a closed space, and this pressure is usually stated to be "irresistible." But the recent discoveries concerning other forms of solid water carry a remarkable corollary, that there may be a definite maximum pressure which cannot be exceeded. This depends on the fact that all the other forms of ice have a *less* specific volume than liquid water. Thus at — 22° and 2,050 atmospheres Ice I changes to Ice III, which is denser than water. Therefore at — 22° the pressure cannot exceed 2,050 atmospheres or approximately 10 tons to the square inch. In the Arctic and Antarctic regions the air temperature often falls far below — 22°, so it is quite possible that Ice III actually exists in nature, sealed up in cavities in rocks. So far, however, it is only known in the laboratory and obviously must remain so. Four other forms of ice have been described, but these are only stable at still higher pressures, in one case only above 6,000 atmospheres and not very much is known about them.[1]

The Phase Rule. Any ordinary substance, for example water, can exist in one single form within a wide though limited range of temperature and pressure, and within this range either the temperature or the pressure can be altered independently without necessarily entailing an alteration of the other. Thus liquid water can exist at any temperature between 0° and 100° and at any pressure. This water is in equilibrium, with no tendency to change its state. Such a system is said to possess two degrees of freedom, or to be divariant. If, however, it is desired to keep ice and water in existence together, that is, in equilibrium, the degree of freedom is less. Thus for example ice and water can coexist at 0° at the atmospheric pressure, but if either the temperature or pressure is altered either all the water will freeze or all the ice will melt, unless an appropriate and corresponding change is made in the pressure or the temperature respectively. Thus an alteration of pressure, for example, carries with it automatically a corresponding change in the freezing point. Such a system thus has only one degree of freedom, since the value of one variable factor is controlled by that of the other. Experiment shows that ice, water and water vapour can continue to exist together in a closed vessel only at one definite temperature and one definite pressure. This constitutes an invariant system. Any change of conditions must cause the disappearance of one or two of the forms. This general principle can be most clearly shown by means of a diagram like Fig. 7, in which the three lines meeting at the point O represent the freezing point and vapour-pressure curves, OC being the freezing point curve, OA the vapour pressure curve for liquid water and OB that for ice. These three curves meet at the triple point O which corresponds to $-0{\cdot}007°$ C. and a pressure of about 4 mm. of mercury. The spaces included between the curves represent the stable fields of existence of water, ice and vapour respectively, and therefore are the loci of divariant systems. All points on the curves represent univariant conditions, and the triple point is invariant. Since the freezing point of water is lowered by pressure the curve OC is inclined towards the pressure axis.

Since in the case here considered there is only one substance present, water, there are only two variables to be considered and the diagram lies in a single plane. If, however, two distinct substances are present, a new variable is introduced, namely the relative amounts, or the *concentration* of the two substances, and a third co-ordinate is required, entailing a solid model in three dimensions. For very many purposes, however, it is convenient to assume atmospheric pressure and to omit the pressure axis, considering only temperature and concentration and representing them by a plane *ct* diagram. A system in which one variable is omitted or assumed to be constant, is called a *condensed system*. Its *ct* diagram may be quite properly regarded as a plane section for a constant pressure of the *ctp* solid model.

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[1] Tammann, *Zeits. phys. Chem.*, vol. lxxxiv, 1913, p. 257. Bridgman, ibid., vol. lxxxvi, 1914, p. 513. Tammann, ibid., vol. lxxxviii, 1914, p. 57. See also p. 79.

As already mentioned, it is quite obvious that some direct relation exists between the number of degrees of freedom in a system and the number of distinct substances that can exist in a state of equilibrium. This relation is expressed in the generalization known as the Phase Rule, first enunciated in a maze of abstract mathematics by Willard Gibbs, and later reduced to a much simpler form by Bakhuis Roozeboom, Van't Hoff and a host of later workers.[1]

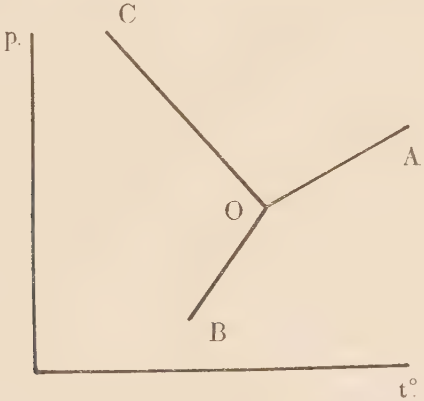

Fig. 7.—Freezing and vapour-pressure curves of water. For explanation see text.

At this point a new terminology must be introduced: in the system just described the only chemical substance present is H_2O, but this can exist in three forms, ice, water and vapour. In a salt solution, on the other hand, there are two different substances, salt and water, which can exist as salt, ice, solution and vapour, four forms altogether, and so on for any number of substances. According to the terminology now universally adopted the different chemical substances are called *components*, the physical forms in which they exist, *phases*. A phase can be defined as a homogeneous, physically distinct and mechanically separable portion of a system. As the components of a system there are to be chosen the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.[1] The other quantity concerned is the number of degrees of freedom, as above defined. Let n be the number of components, p the number of phases and f the number of degrees of freedom, then in its full form the Phase Rule is expressed by the equation

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[1] For a general account see Findlay, *The Phase Rule*, 5th edition, London, 1923.

$$f = n - p + 2.$$

In the case of a condensed system, where one degree of freedom is omitted, this of course reduces to

$$f = n - p + 1.$$

Thus in the instances just referred to, it is seen that water constitutes a system of one component capable of existing in three phases: here at the triple point

$$f = 1 - 3 + 2 = 0$$

and the system is invariant. In a salt solution there are two components, water and salt: at an invariant point the condition must be fulfilled that

$$2 - p + 2 = 0$$

therefore $p = 4$, and there must be four phases present, namely ice, salt, solution and vapour. In general terms, at an invariant point the number of phases must exceed the number of components by two. It must be understood that polymorphic forms of the same compound are to be regarded as different phases: so also a hydrated and an anhydrous form of the same salt are different phases.

Sometimes a difficulty is found in determining the number of components, as in the well-known case of the dissociation

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Here there are three phases, two solids and one gas: so long as neither of the products of the dissociation is removed from the system the above equation holds and by the rule just given there are two components, CaO and CO_2: if, however, the ratio of these is altered it would be necessary to choose as components $CaCO_3$ and either CaO or CO_2, whichever was in excess; still two components, but different ones. If at any point in the reaction all the CO_2 were removed the system would consist of $x\text{CaCO}_3 + y\text{CaO}$. On further heating this would break up as follows:

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[1] Findlay, *loc. cit.*, pp. 6 and 8.

$$\begin{aligned} x\text{CaCO}_3 + y\text{CaO} &= x\text{CaO} + y\text{CaO} + x\text{CO}_2 \\ &= (x + y)\ \text{CaO} + x\text{CO}_2 \end{aligned}$$

Nothing new appears on the right-hand side of this equation, since

$$x\text{CaO}+x\text{CO}_2 = x\text{CaCO}_3$$

leaving $\{(x + y) - x\}$CaO as the second component. Similar principles can be applied in other doubtful cases: this one has been mentioned here because it is of importance in the theory of metamorphism of limestones.

CHAPTER II

FUSION AND SOLIDIFICATION—SOLUTIONS

Melting and Freezing. Since the transformations of matter from a liquid to a solid state or vice versa are of the very greatest importance in many geological and mineralogical processes, including the formation of the igneous rocks and of a great number of mineral deposits of commercial value, no apology is offered for a rather detailed consideration of the subject. It may probably be said with truth that as a process of mineral formation crystallization from fusion is only second in importance to crystallization from solution. The two processes are in point of fact most closely connected, but as the study of anhydrous melts is in some ways simpler than that of solutions, it will be considered first.

It has already been shown that if a fused mass is cooled too rapidly for the establishment of a stable equilibrium, crystals may fail to form. This, however, does not apply to all classes of substances ; metals and sulphides, for example, are, so far as is known, invariably crystalline, however quickly they may be cooled. Therefore the consolidation of such substances is always accompanied by a thermal change in the system, which may not be the case in silicate melts for example. It is with fusion and solidification of this type that this section is concerned.

In dealing with this subject there are several facts to consider. In the first place most crystalline substances, and as we have reason to believe all crystalline substances when heated to the appropriate temperature, are converted to a liquid or amorphous form, higher pressures being sometimes necessary to prevent sublimation. Under a given pressure the melting point of a solid is fixed : it is a physical constant for that substance. It was until lately believed that it was impossible for a crystalline substance to retain its structure above the melting point, that is to say that superheating or delayed equilibrium could not occur. Some recent work by Bowen on the melting of the felspars has thrown doubt on the universality of this supposed law, but it is in any case a very rare phenomenon, only occurring in substances that form a very viscous liquid. Secondly fusion or crystallization is accompanied by a change of volume.[1] Thirdly, the change of state is always accompanied by a heat effect. It is believed that the change from the liquid to the solid form always involves evolution of heat and vice versa; although it has been suggested that the inverse is theoretically possible, yet no such case is known. Lastly experiment shows that freezing and melting points are altered by pressure. This last statement can also be deduced theoretically from thermodynamic principles and can be stated in simple language in the following way. When a substance expands on melting an increase of pressure will tend to counteract the expansion; therefore it is necessary to put more energy into it to overcome the pressure: this energy is supplied by an increase of heat, therefore the melting point is raised by pressure. This is the almost universal case: among the common substances only the freezing point of water is lowered by pressure.

All the facts mentioned in the last paragraph are intimately connected; so much so that if the numerical values of the thermal effect and of the change of volume are known the raising or lowering of the freezing point can be calculated, by means of the Clausius-Clapeyron equation, as follows:—

$$\frac{dt}{dp} = \frac{T(\overset{V_L}{v_2} - \overset{V_S}{v_1})}{L}$$

Here T is the absolute temperature, v_2 and v_1 the volumes of the liquid and solid respectively and L the latent heat in calories. Since v_1 may be greater or less than v_2, it is clear that the change of freezing point may have either a positive or negative sign; i.e. the freezing point may be raised or lowered. The actual value is usually very small; for most minerals so far as is known it amounts to about 0·09° C. per atmosphere: for water it is only about 0·007° C. and is negative.

Here comes in a consideration of great importance in the theory of petrogenesis. In all rock-forming minerals v_2 is greater than v_1 and the freezing point is raised by pressure. But liquids are more compressible than solids, and as the pressure is raised the value of $(v_2 - v_1)$ will decrease. This means that the freezing point curve will be convex to the pressure axis and when $v_2 = v_1$ the curve will pass through a maximum. According to Tammann[2] this condition has been realized with some organic substances, and in all probability at the enormous pressures prevailing within the earth the same is true of minerals. In order to account for the high rigidity of the earth as a whole, in spite of the high temperatures that appear to prevail in depth many geologists and geophysicists have assumed an almost unlimited raising of the freezing-point of minerals by pressure, so that the globe as a whole is solid : this subject cannot be pursued here in detail, but it is clear that this assumption is in need of revision.

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[1] For a special case where this is not true, viz. at a certain definite pressure, see below.

[2] *Kristallisieren und Schmelzen*, Leipzig, 1903, p. 95.

In the case of water and ice I $(v_2 - v_1)$ is negative, and the freezing point curve is therefore as shown in Fig. 9. From the theoretical point of view it appears justifiable to regard water and the small group of metals that behave in the same way as substances which under the ordinary range of temperature and pressure are represented by the portions of their freezing point curves beyond the maximum, corresponding to MN in Fig. 8. Since at higher pressures and lower temperatures ice inverts to other crystalline forms this assumption cannot be tested either by theory or experiment.[1]

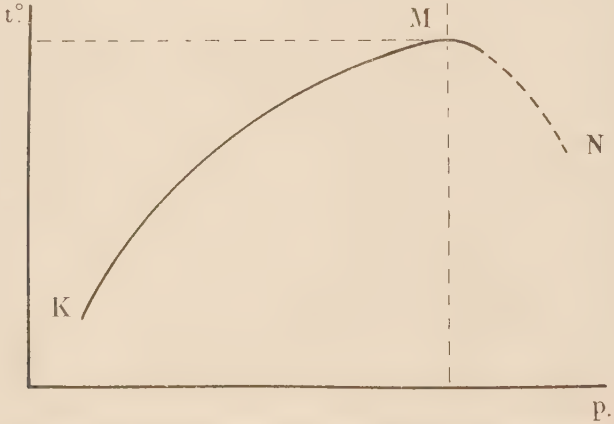

Fig. 8.—Diagram to show raising of freezing point by pressure up to the maximum M, where $v_2 - v_1 = 0$.

Hitherto it has been assumed in this discussion that the solid and the liquid resulting from its fusion have the same composition, but this is not always the case. Some substances at their melting point break up into another solid of a different composition and a liquid. The newly formed solid must in this case necessarily have a higher melting point than the other. This is called incongruent melting. It occurs in some common silicates of the igneous and metamorphic rocks, as will appear later (see p. 119).

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[1] Since water at the lowest attainable pressure (i.e. in a vacuum) still behaves as usual this idea involves the somewhat metaphysical conception of negative pressure on the left-hand portion of the curve, and must not therefore be taken too seriously in the present state of our knowledge.

The Freezing of Binary Systems. Up to this point attention has been confined to the fusion and crystallization of simple and homogeneous substances, to systems of one component. Of far greater importance, however, in geology and mineralogy are the more complex systems of two or more components. In this section a brief account will be given of the possible types of crystallization shown by binary systems, it being assumed that in all cases there is only a single homogeneous liquid phase. In this class several types of freezing are possible, according to whether the solid products of consolidation can or cannot form homogeneous mixtures. Here we come up against a new conception of the highest degree of importance in this subject, namely the phenomenon variously known as isomorphism, solid solution, or the formation of mixed crystals. All these expressions are essentially names for the same thing, which can also be stated, in other words, as a homogeneous solid phase. Two solids may be either completely immiscible, partially miscible, or completely miscible in any proportions, and the form of the freezing-point diagram is different and characteristic in each case. The condition of complete immiscibility is by far the most simple and will be studied first.

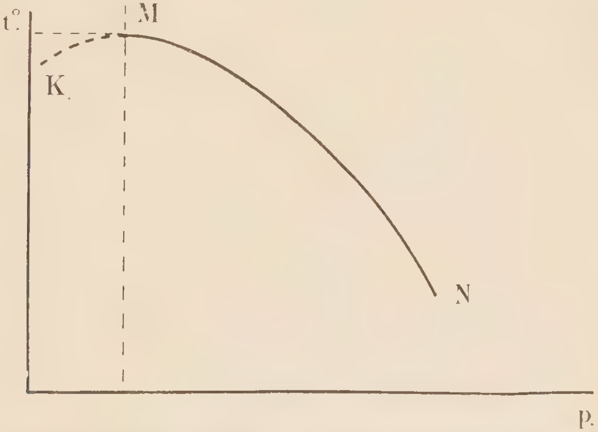

FIG. 9.—Diagram to show lowering of freezing point by pressure, where $v_2 - v_1$ is negative.

It is a matter of observation and experiment that the addition to a liquid of a substance soluble in it lowers the freezing point of the liquid. Thus salt water freezes at a lower temperature than fresh water, and experiment shows that the lowering of the freezing point is proportional to the amount added. Moreover solution is always attended by some thermal effect, either evolution or absorption of heat, and by change of volume, either expansion or contraction. If the latent heat of fusion of the solvent is known the lowering of the freezing point of a pure substance A by the addition of a small quantity of another substance B soluble in it can be calculated by means of Van't Hoff's equation: for one molecular weight in grams of B dissolved in 100 grams of A the equation takes the following form.

$$\Delta t = \frac{0{\cdot}0198T^2}{Q} \text{ or approximately } = \frac{0{\cdot}02T^2}{Q}$$

where T is the freezing point of A in degrees absolute (C.° + 273) and Q is its latent heat of fusion. The lowering of the freezing point is therefore independent of the nature of the dissolved substance, but it is an essential condition that mixed crystals are not formed.

If now we start with two pure substances A and B, fulfilling this condition and completely miscible in the liquid state, each of them when added to the other will progressively lower its freezing point. A diagram can then be constructed with percentages of A and B in the mixture as abscissæ and freezing points as ordinates. Evidently two curves will be obtained, which must eventually intersect (Fig. 10). This point of intersection represents the composition of the mixture of A and B having the lowest possible freezing point, and is called the *eutectic point*: a perpendicular dropped from it to the concentration axis gives the percentage composition of this mixture, the eutectic ratio, and a horizontal line through it gives the eutectic temperature. The two freezing-point curves are not generally straight lines, but slightly curved.

Let us now consider the course of cooling of a liquid mixture represented by any point p in Fig. 10, to the left of E. As the temperature falls the mixture remains liquid till it reaches q: at this point it is saturated for the substance A, or in other words it reaches the equilibrium curve for the melt and solid A: therefore A begins to separate. Consequently the concentration of the melt changes, and as the temperature continues to fall the system moves along the line qE. When it reaches E it cuts the equilibrium curve for solid B and the melt; therefore B also begins to crystalsize and A and B crystallize out together as the eutectic mixture of constant composition, the final result being crystals of *A* embedded in a conglomerate of *A* and *B*. If the starting point is chosen on the right of *E*, the course of events is precisely similar except that crystals of *B* form first: the final eutectic is the same. An important conclusion to be drawn here is that the order of crystallization of two minerals from a mixed melt is independent of their absolute freezing points from a pure melt, and depends only on their relative concentration in the mixture. This conclusion, which applies equally to more complex systems, disposes of many statements current in petrological textbooks as to the supposed "Normal Order of Crystallization" in igneous rocks, a law founded merely on empirical observation and admittedly showing many exceptions.

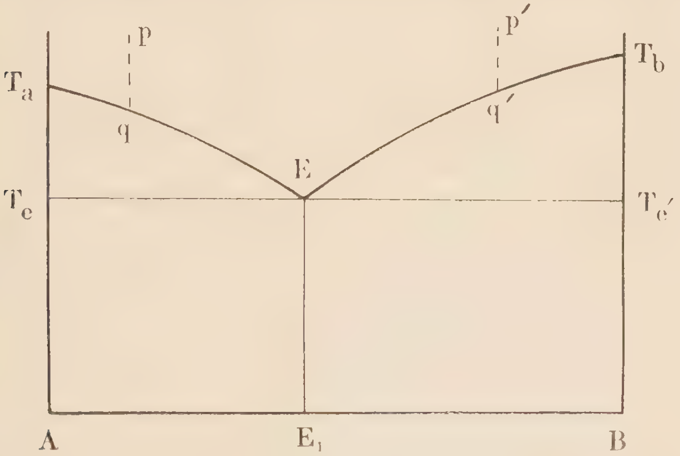

Fig. 10.—Normal eutectic diagram in the complete absence of solid solution. For explanation see text.

The fact that the common rock-forming minerals do commonly crystallize in a more or less definite order is due to the circumstance that igneous magmas actually vary within somewhat narrow limits, so that conditions are also fairly uniform.

A eutectic mixture also possesses one special property, in that it crystallizes at constant temperature, like a pure substance. The cooling curve of a eutectic mixture will therefore show a horizontal portion, called the eutectic arrest. The curve will therefore be similar in form to Fig. 3. There is this difference, however, that the length of the arrest depends on the actual amount of the eutectic formed. It will therefore be longest at *E*, where the whole solidifies as the eutectic, and will vanish at *A* and *B*, where no eutectic is formed. Thus by taking the cooling curves of varying mixtures of the two substances and plotting the length of the arrest as vertical ordinates in the eutectic diagram (Fig. 11) a valuable check is obtained on the correctness of the freezing point curve and the position of its inflection point. This method is much used in metallography.[1]

We must now consider rather more fully the meaning of the different parts of the diagram Fig. 10. Above the line T_aET_b only a homogeneous liquid phase can exist : below the horizontal line $T_eET_{\acute{e}}$ only solids are stable. Within the triangles T_aET_e and $T_bET_{\acute{e}}$ liquid can exist along with solid A or solid B respectively. As before stated the broken curve T_aET_b represents the equilibrium conditions for the pure solids and liquid. These facts are indicated in Fig. 12. It is evident that both solid A and solid B cannot at once be in equilibrium with the same liquid, except at the eutectic point.

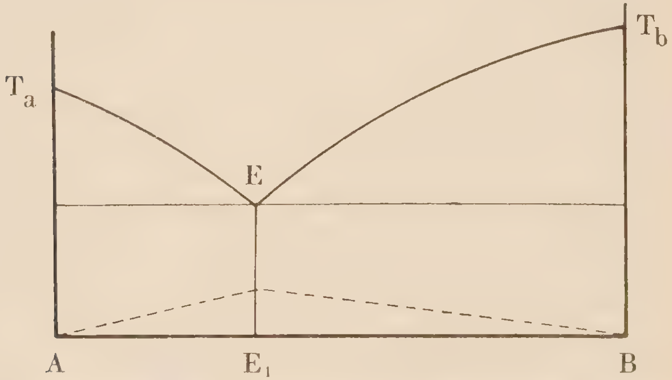

Fig. 11.—Similar to Fig. 10, but showing the eutectic arrest (dotted line) as obtained from cooling curves.

In this description no account has been taken of the effect of pressure and as here described this is an example of a condensed system, but pressure does have an effect in displacing both the freezing point curves and the composition of the eutectic. If a pressure axis is added to the diagram at right angles to the others a solid model is obtained showing freezing point surfaces and a eutectic line. The effect of pressure, however, is in reality very small.

It has been shown by Vogt that given certain physical constants of the two substances A and B, namely, their freezing points, latent heat of fusion, molecular weight and degree of electrolytic dissociation the position of the eutectic point can be calculated: the equations are extremely complicated and will not be given here, but certain general conclusions can be stated: (1) if the two freezing points are nearly equal the eutectic point will lie nearly in the middle; if the difference is great, it will lie considerably nearer the substance with the lower freezing point: (2) other things being equal the eutectic point will lie nearer the component with the lower latent heat: (3) if the component of lower freezing point has a conspicuously higher molecular weight, the eutectic point will lie still nearer to it.[1]

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[1] See Desch, *Metallography*, 3rd edition, London, 1922, p. 18.

In this discussion it has been tacitly assumed that supersaturation (undercooling) does not occur, but this is not always the case.

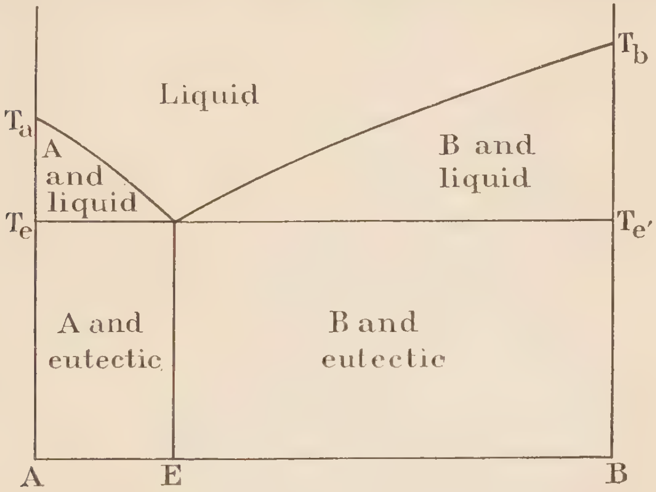

FIG. 12.—The fields of existence of liquid and crystals in a normal eutectic diagram.

The melt may be supersaturated for one or other or both of the components and then various false equilibria may be established. In Fig. 13 let the broken lines represent the possible limits of supersaturation: then it is clear that there may be no less than three pseudo-eutectics in addition to the real one, and owing to evolution of heat on crystallization from the undercooled melt at *F*, *G*, or *H* very complicated effects might be produced both in the cooling curves and in the order of the minerals.

Intermolecular Compounds. It is often the case that two substances though not miscible in all proportions in the solid state, can yet combine in certain definite proportions to form stoichiometric compounds of the type A_mB_n. This behaviour is very common for example among the sulphide ores and the metallic alloys.[1] Such intermolecular compounds have fixed physical properties, including a definite freezing point, which is entirely independent of the freezing points of either of its components, and is not in any case the arithmetical mean between them, but may be higher or lower, usually the former: indeed, cases are known where the freezing point of the compound is much higher than that of either of the components. In the absence of solid solution the compound A_mB_n behaves just like A or B; it lowers the freezing points of A and B and its own freezing point is lowered by them; eutectics can be formed with each, and the position of the compound on the concentration axis always corresponds to a maximum on the freezing-point curve, which in point of fact resembles two eutectic diagrams placed side by side, except that the top of the curve at the compound is always smoothed off, the two branches not cutting the ordinate at an acute angle, as they do at the pure component ordinates. Fig. 14 shows with sufficient clearness the various fields of stability possible in this case. In some instances a large number of molecular compounds are formed, e.g. many metallic alloys, in different ratios and the curves become very complicated.[2] Many complex silver and copper ores belong here.

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[1] Vogt, *Die Silikatschmelzlösungen*, Kristiania, 1904, vol. II, p. 128.

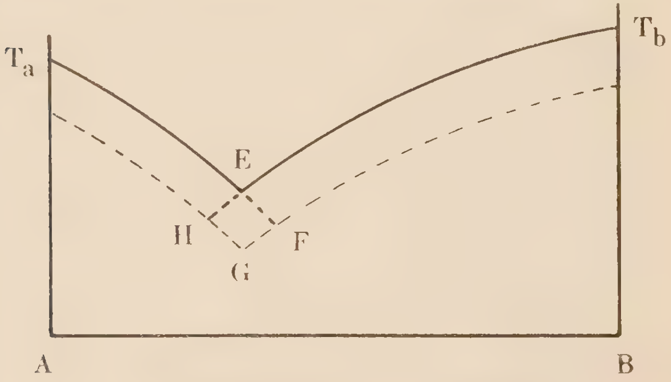

FIG. 13.—False equilibria due to supersaturation.

From the diagram it is obvious that the compound A_mB_n must be found, either as crystals of earlier consolidation or as a constituent of the eutectic, in every possible mixture of A and B, a point of some importance in mineralography. There can be no simple mechanical mixture of A and B.

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[1] See Desch, *Intermetallic Compounds*, London, 1914.

[2] For many details and references see Desch, *Metallography*, 3rd edition, London, 1922, especially the Appendix.

Crystallization with Unlimited Solid Solution : Complete Isomorphism. It will be most convenient to consider this type next, although perhaps logically the case of partial solid solution should come first : this however is more complex, and will be better understood when the principle of complete solid solution has been studied. Here the ruling condition is that the two components A and B are completely miscible both in the liquid and the solid state. It can then be proved thermodynamically and shown by experiment that no pure component can separate from a mixture ; that the liquid and solid in equilibrium at a given point have different concentrations and that the curves indicating freezing and melting must be continuous and cannot intersect at sharp angles. Since the solid and liquid have different compositions, there must be *two* curves, called the *solidus* and the *liquidus* curves ; these are also to be regarded in a sense as melting-point and freezing-point curves, as will appear later. All the curves are continuous, without breaks, as before said, but three cases present themselves :

(*a*) The curves lie wholly between the freezing points of the components :

(*b*) The curves show a maximum :

(*c*) The curves show a minimum.

These three cases are illustrated in Fig. 15. The first is by far

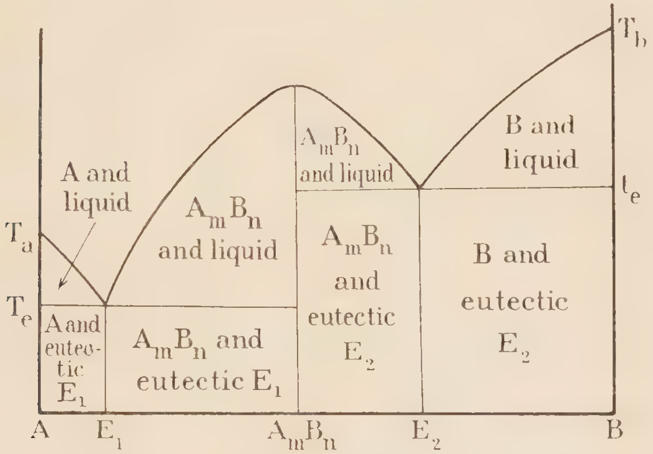

FIG. 14.—Eutectic diagram for the case where an intermolecular compound is formed. No solid solution.

the commonest: case (*b*) is apparently not known in minerals, while (*c*) is rare. Only case (*a*) will be considered in detail.[1]

Let *A* and *B* be two substances with complete mutual solubility both in the liquid and the solid state: and let the liquidus and solidus curves lie entirely between their melting points. The diagram will then have the form shown in Fig. 16. The meaning of the two curves can be explained as follows: starting with a melt having the composition and temperature represented by *p*

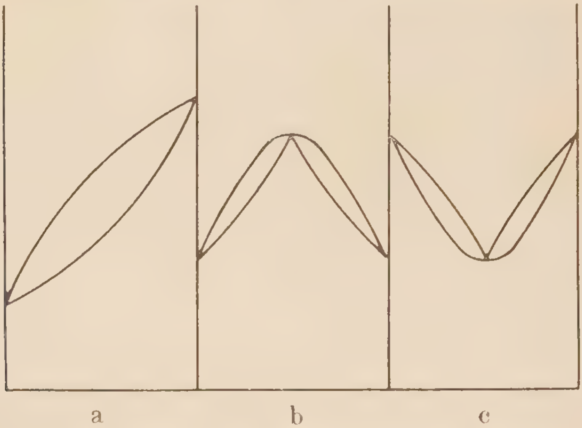

FIG. 15.—The three possible forms of liquidus-solidus curves for complete isomorphism in the solid (complete solid solution).

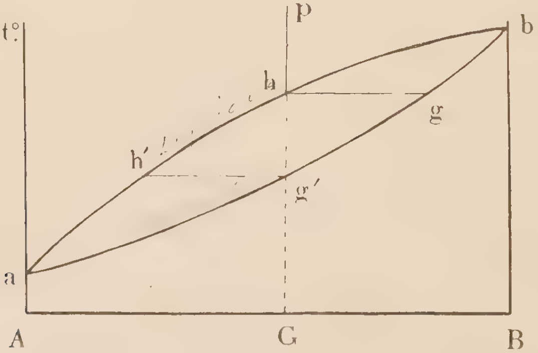

FIG. 16.—Liquidus-solidus curves for complete solid solution, type *a*.

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[1] For a theoretical proof of the relations here empirically stated see for example Whetham, *The Theory of Solutions*, Cambridge, 1902, where the curves are derived from functions of the thermodynamic potential.

and cooling slowly, when the temperature reaches h a solid will begin to separate having the composition shown by drawing a horizontal (isothermal) line to cut the solidus curve in g. The points h and g then represent the liquid and solid in equilibrium at the temperature shown by the line hg. However, the separation of an appreciable quantity of g alters the composition of the melt, so that g is no longer in equilibrium with it ; g now contains an excess of B, which will be leached out and return to the liquid. But as the temperature falls more and more solid must separate causing the indicating point h to move along hh' while correspondingly g moves along gg'. The last drop of liquid will have the composition h', and when g reaches g' it will be found that the whole mass is a solid of the uniform composition G, which is the same as that of the initial liquid. This is known as the Principle of Continuous Reaction,[1] since a reaction is continually in progress between solid and liquid so long as any liquid exists.

It must, however, be very strongly emphasized that the process only takes place in this ideal manner if the cooling is so slow that ample time is allowed for the establishment of equilibrium at every stage. This condition is specially difficult of attainment in the silicates, owing to the viscosity of the liquid near the freezing point. When equilibrium is not fully attained the core of the first formed crystals will contain too much B and the outer layers too much A, leading to the formation of zoned crystals, as is so often seen in the plagioclase felspars. The subject will be referred to again in connection with this group of minerals.

The most notable feature of this type of system is that crystallization does not wholly occur at a definite temperature as in the consolidation of a pure substance or of a eutectic, but extends over a temperature interval—as shown by the distance between the points h and g' in Fig. 16. When a mixture of composition G is cooled from a state of fusion, the formation of crystals begins at h and ends at g' : conversely on heating a solid mixture G, melting begins at g' and is complete at h. This crystallization or melting interval is characteristic of solid solutions, and serves to distinguish them from definite compounds or eutectics which show a horizontal arrest on the cooling curve.

Limited Solid Solution. Many cases are known and many more suspected where two mineral compounds are capable of forming mixed crystals only to a limited extent, each being able to dissolve a small amount of the other, and intermediate compounds being impossible. Under the conditions here postulated therefore a eutectic can be formed in this insolubility interval, whereas within the limits of solubility the two components behave much as in the last described type, but only up to the limits. Hence the liquidus-solidus diagram is in a sense a combination of this type with the eutectiferous type. However, as will appear shortly, the eutectic is not a conglomerate of the pure substances, but of two kinds of mixed crystals. The complete diagram has the form shown in Fig 17. *AB* as usual represents concentration in percentages, T_a and T_b freezing points of pure *A* and *B*, $t_1 t_2$ the eutectic temperature below which liquid in equilibrium with solid cannot exist. If now we start with a liquid at *p* and cool, the first solid to separate will be *q*, and as before a continuous reaction sets in, so that when *p* reaches *E*, *q* will have arrived at *F*. This point *F* represents the maximum amount of *A* that can be dissolved by solid *B* at that temperature; it is a saturated solid solution in equilibrium with the liquid of eutectic composition *E*. Similarly if the starting point were on the other side of *E* the final solid would be *D*, a saturated solution of solid *B* in solid *A*. The eutectic that then forms is made up of a conglomerate of *D* and *F*, since both of these, and only these, are in equilibrium with liquid *E* at the eutectic temperature. Hence the result will be mixed crystals of earlier consolidation, either *D* or *F*, embedded in a conglomerate of *D* and *F*. No pure compounds can separate from such a system. The two diverging lines *DG* and *FH* mean that as the temperature falls the mutual solid solubility decreases and the crystals of compositions *D* and *F* may undergo further changes with separation

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[1] Bowen, *Journ. Geol.*, vol. xxx, 1922, pp. 177–198.

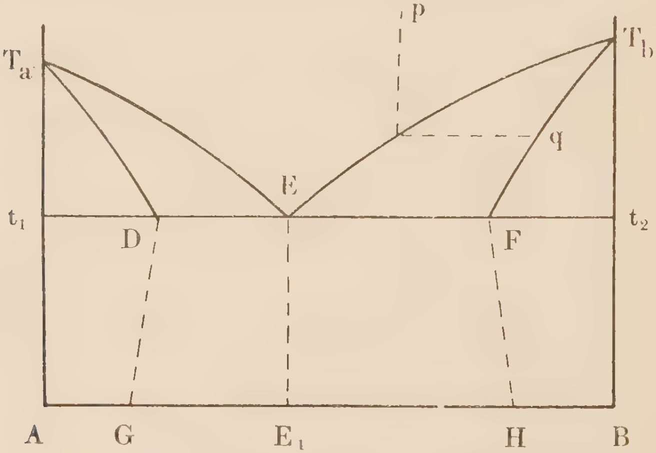

FIG. 17.—Partial solid solution. Explanation in text.

of enclosures of *A* or *B*, leading to various characteristic structures usually called intergrowths, though they are really separation products. The well-known perthitic structures in the alkali felspars apparently belong here.

It has been suggested that the possibility of this type of system depends upon the fact that both *A* and *B* are actually dimorphous substances, but that one form of each is unstable below a certain temperature. The whole diagram would then be represented by two pairs of curves like Fig. 16, arranged as shown in Fig. 18, all the dotted portion below the intersection of the two liquidus curves being unstable. Thus A_1 is completely isomorphous with B_1, and A_2 with B_2, but A_2 and B_1 have only limited miscibility. This idea, though plausible, is purely speculative.

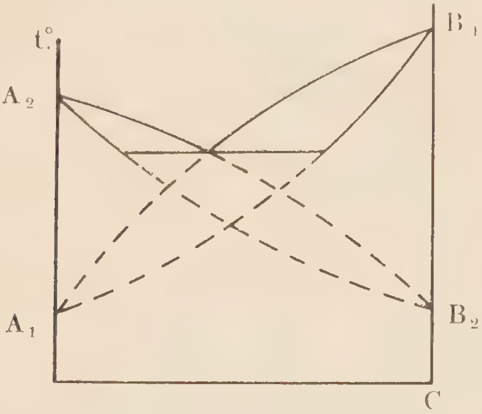

FIG. 18.—Theoretical explanation of the type of curves shown in Fig. 17. See text.

It can be shown theoretically that another type of liquidus-solidus curve is possible in cases where one of the substances concerned undergoes an inversion to another polymorphous form at a certain temperature between the freezing points of the two pure components. As the subject of inversions and polymorphism has not yet been touched upon, consideration of this case is postponed.

Limited Miscibility in Liquid Phases. In all the cases yet described it has been stated or assumed that at all temperatures above the freezing-point curve only a single homogeneous liquid phase could exist, but this is by no means always the case. The opposite holds true of a number of binary systems, some of which are of importance in geology and in industry. Many pairs of metals are completely miscible when fused, but lead and tin when melted together in equal quantities separate into two layers. This same effect in the case of metals or sulphides and silicates is the foundation of the separation of metals or mattes from slags in all metallurgical processes, and it is believed that the formation of certain ore deposits is to be attributed to the same cause operating in nature.

The mutual behaviour of any pair of liquids can be assigned to three types, which are connected by a complete series of intermediate forms. The extreme case of complete immiscibility is represented by the behaviour of oil and water: an emulsion can be formed by vigorous agitation, but no true solution: the other extreme is complete miscibility in any proportion, as shown by water and alcohol. Between these and linking them together are the numerous instances, like phenol or ether and water, where a mixture, after stirring or shaking, separates into two layers, each of which has dissolved a little of the other. This mutual solubility increases with the temperature, until at last a point is reached above which the liquids are soluble or miscible in all proportions. Thus is obtained a solubility curve of the type shown in Fig. 19, in which the abscissæ are as usual concentrations and the ordinates temperatures. A mixture represented by a point such as x, will split into two layers, represented by y and z, called conjugate liquids; the lighter will naturally float on top of the heavier. If the temperature is raised each solution dissolves more of the other constituent and the indicating points travel along yK and zK till they meet at K; above this point, which is called the critical solution temperature there is only one homogeneous liquid phase. If the tempera-

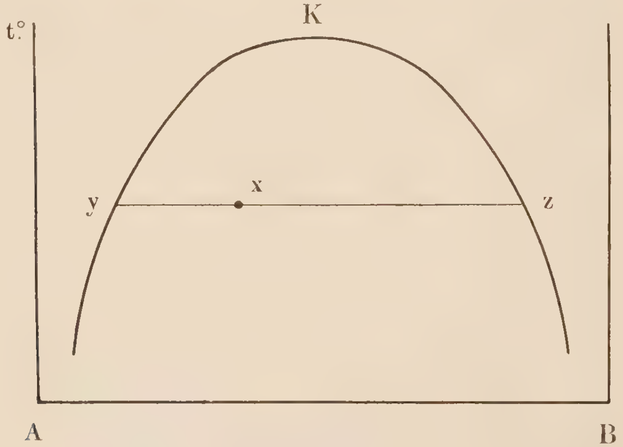

FIG. 19.—Solubility curve for two partially miscible liquids.

ture falls the mutual solubility decreases, but it is rare for the solubilities to become zero before the freezing point of either liquid phase is reached.

In the most general case the complete diagram is as shown in Fig. 20. Here it is assumed that partial solid solutions can be formed, and that the solid solubility also decreases with fall of temperature. The case of partial liquid miscibility and complete solid solubility is perhaps theoretically possible, but has not been investigated. Its existence is highly improbable. The resemblance in some ways of this diagram to Fig. 17 is obvious.

Starting with a fused mixture represented by x, this on cooling

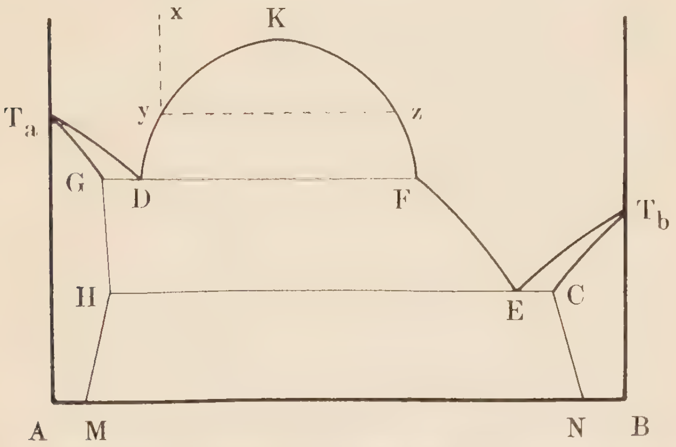

FIG. 20.—Equilibrium diagram for limited miscibility in the liquid state with solid solution.

down till it reaches the curve DKF will then split into two conjugate solutions y and z: on continued cooling these travel along yD and zF. At D the solid solution, represented by the point G, begins to separate and the composition of this liquid changes at constant temperature along the line DF; when it reaches F the last drop of liquid D will disappear and only one liquid F is left. From F to E solid G continues to separate, till at E the eutectic point is reached, resulting in a conglomerate of G and C. The meaning of the lines GHM and CN is the same as before explained in Fig. 17. If the density of the first solid to separate at G is greater than the mean density of the mass it may sink to the bottom, if less, it may rise to the top. Frequently, however, it appears that the viscosity of one or other of the liquids y and z is so great that after their separation drops of one may remain suspended mechanically in the other:

this results, after cooling, in solid inclusions, as for example, of metal in slag, and of slag in metal. Theoretically, however, the liquids separate into two layers. On continued cooling, each proceeds to crystallize as an independent entity, thus leading to a stratification of the mass: in metallurgical processes mechanical separation is effected artificially as near as possible to but just above the temperature indicated by the line *GDF*, in order to minimize the loss of metal in the slag. This diagram can be simplified somewhat by ignoring the existence of solid solutions, but is not then true to nature (Fig. 21). In this diagram it is assumed that only pure *A* and pure *B* can form from the mixture, but this is rarely the case. From what has already been said the course of crystallization of such a system as *x* will be obvious. The chief difference is that the points corresponding to *G* and *C* lie on the *A* and *B* ordinates. In both diagrams no single solution can exist represented by any point within the curved areas *DKF*. Anywhere above T_aDKFET_b a single liquid phase is stable, while below *GDFEC* only solid is stable. A point such as *w* to the right of *F* cannot give rise to two liquid phases.

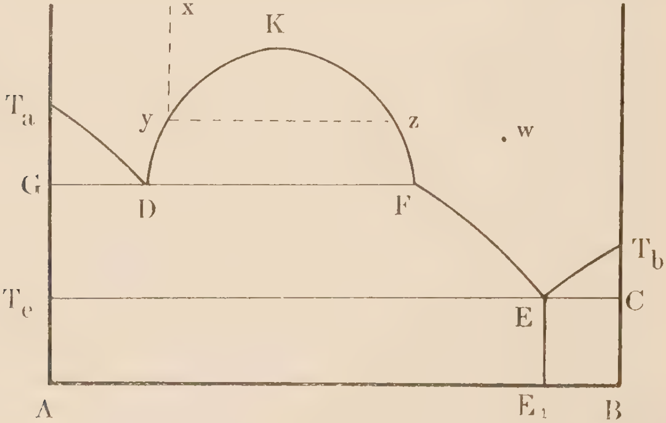

FIG. 21.—Equilibrium diagram for partial miscibility in the liquid state, but no solid solution.

Ternary Systems. Hitherto attention has been confined to various types of systems of not more than two components. But in nature systems of a higher degree are very abundant. A short sketch will here be given only of some of the simpler types of systems of three components, since many of these are of great theoretical interest and of industrial importance. Further it is possible to give in a comparatively simple form graphic representations of the thermal relations of such systems, a matter which becomes much more difficult in quaternary systems and almost impossible in those of higher order, since intelligible representations of four-dimensional space are as yet hardly attainable.

First is to be considered the method of representing on a plane diagram the concentration of a three component system. This is now almost universally effected by a figure in the form of an equilateral triangle, which is in reality a system of three co-ordinates inclined at 60° to one another. A method now very rarely used is to employ a right-angled triangle: this has not been found satisfactory. In such an equilateral diagram the points representing the composition of the pure components are naturally placed at the corners, but there are two methods of graduating the axes. Since it is desired to represent percentages, the scale of division chosen must necessarily be into 100 parts and fractions are usually estimated, unless the diagram is on a very large scale. There are two methods in general use: in one the sides of the triangle are divided into 100 parts; in the other the scale is marked along the perpendiculars let fall from the apices on to the opposite sides. The first method will here be used.

The method of plotting a given percentage composition, for instance $A=45$ per cent., $B=30$ per cent., $C=25$ per cent., is as follows. Along one side of the triangle, for preference the base, mark off from B towards A a distance Ba equal to the percentage of A, and from A towards B mark off Ab the percentage of B: the distance ba must then obviously be the percentage of C. Through a and b draw lines parallel to the other sides of the triangle: the intersection of these lines gives the point required. A formal proof is scarcely necessary.

Here a special property of the equilateral triangle must be noted. If a line is drawn from C to any point on AB, every point on that line represents a mixture of A, B, and C, in which the ratio of A to B is constant, only the proportion of C being variable. Hence such a line can be taken as representing a binary system in which the components are A_xB_y and C. This idea is often useful in complicated systems.

On the basis of a concentration diagram of this kind it is easy to construct a model to represent some function of the composition, such as freezing-point, by erecting at the proper points perpendiculars proportional to the quantity in question. If enough perpendiculars are thus obtained a sheet can be imagined as resting on their tops, thus representing the variations of the freezing point by a surface, which may be continuous in smooth curves, or made up of distinct portions intersecting in ridges or furrows: the last named is the commoner case, owing to the law of depression of freezing point. It follows that the highest verticals are usually at *A*, *B* and *C*, the surfaces sloping away from these points, but peaks or ridges may be found anywhere. Several different and characteristic forms of surface are possible. It is obvious that the lines of intersection of these surfaces can be projected down on to the plane triangle, which will then contain straight or curved lines, intersecting each other and the sides of the triangle in points, which points are important elements in the thermal diagram of the system.

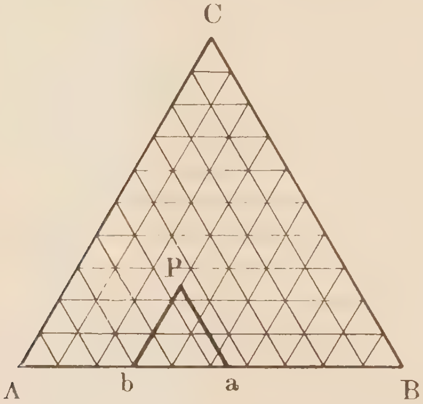

FIG. 22.—Method of plotting the composition of a ternary mixture, as explained in the text.

Types of Ternary Systems. The first thing to be noted is that every ternary system *ABC* is composed of three binary systems *AB*, *BC* and *AC*. Each one of these binary systems must belong to one or other of the types already described, and the theory of ternary systems consists mainly in working out the results that must follow from the different possible combinations of these types. Only three or four simple cases will here be attempted, as the subject obviously can become very complex.

Case 1. All the components are completely miscible in the liquid state and completely immiscible either in pairs or all together in the solid state. Here obviously all the binary systems must belong to the simple eutectiferous type (p. 27). Furthermore the presence of the third component will in all cases lower the eutectic point of the binary systems and modify the relative proportions of the components in them, in such a way that all three " eutectic curves " must meet in a point at a lower temperature than any of the three binary eutectics. The ternary eutectic must be the lowest point in the freezing-point surface, and three "eutectic gutters" will converge at it. The three pairs of converging surfaces each look rather like the wings of a butterfly and a sketch of the whole model rather resembles some impracticable form of flying machine, as shown in Fig. 24.

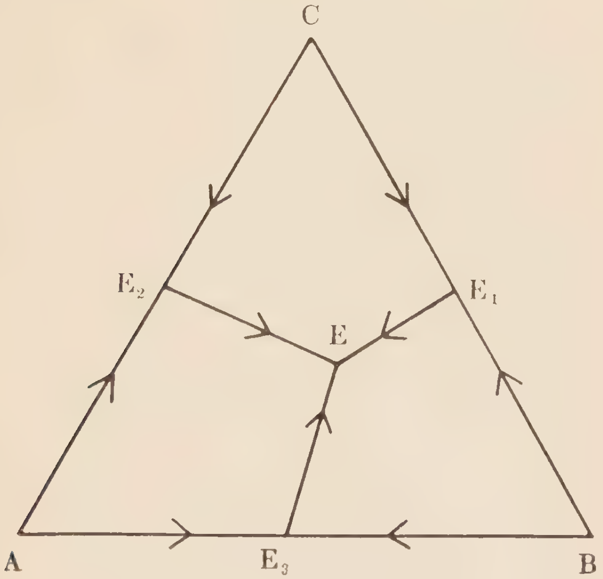

FIG. 23.—Eutectic diagram for a ternary mixture, when no compounds are formed between the components *A*, *B*, *C*.

The arrows show the direction of downward slope of the lines in the model, which is here projected on its base.

It is possible, however, to represent such a model on a plane diagram in a very satisfactory manner by means of isothermal contour lines. This term scarcely requires explanation. Fig. 25 shows an example of such a contoured diagram.

We must now follow the course of crystallization in such a ternary system, as represented for example by a potential mixture of quartz, felspar and mica in a hypothetically simple granite magma. For convenience they may still be called *A*, *B* and *C*. Starting with such a point as *x* in Fig. 26 the order of crystallization may be worked out as follows. The point *x* evidently indicates a proportion of *C* in excess of the eutectic ratio. From *C* draw a line through *x* to cut the nearest binary curve in *y*. Along *xy* pure *C* will crystallize, but at *y* the solution is saturated for *B*, which also begins to crystal-

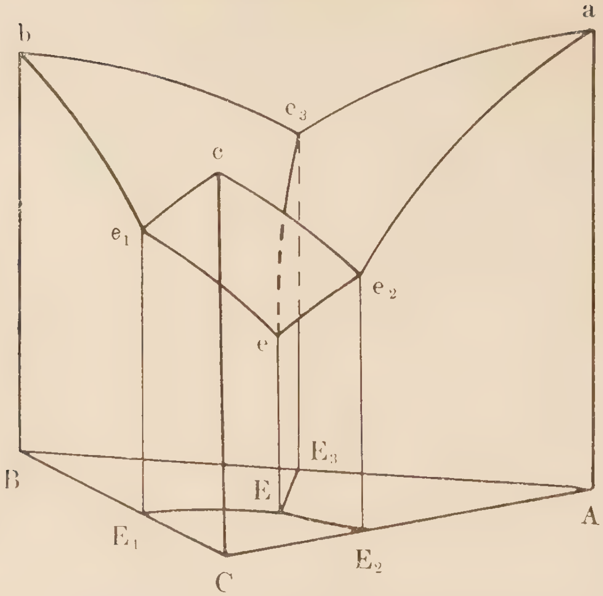

FIG. 24.—Model of ternary eutectic surfaces.
(After Harker, *The Natural History of the Igneous Rocks.*)

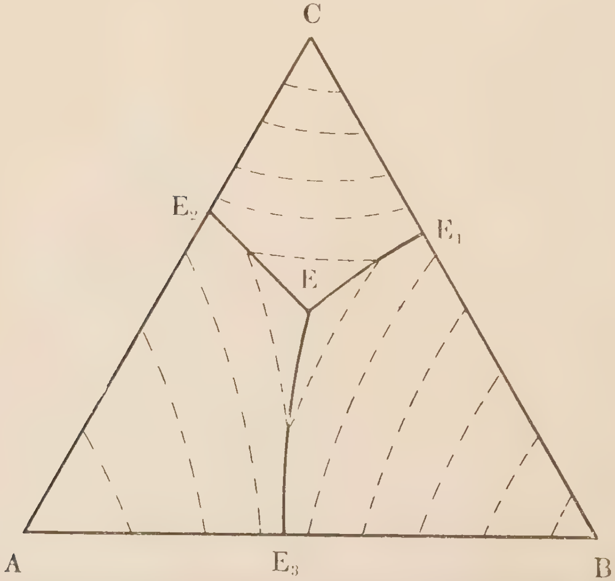

FIG 25.—Ternary eutectic system of the same type as in Figs. 23 and 24 shown by means of contour-lines (isotherms).

lize, therefore the indicating point now turns along yE, with concurrent crystallization of C and B until the composition reaches the ternary eutectic point E, when all three minerals crystallize together. The order is therefore C, $C+B$, $C+B+A$, or in general terms C,B,A. In Fig. 23 the arrows show the directions of falling temperature, and every solution represented by a point *within* the triangle must end in the formation of the ternary eutectic, the amount of it being smaller the nearer the starting point is to the sides of the triangle.

Case II. One pair of components are completely isomorphous,

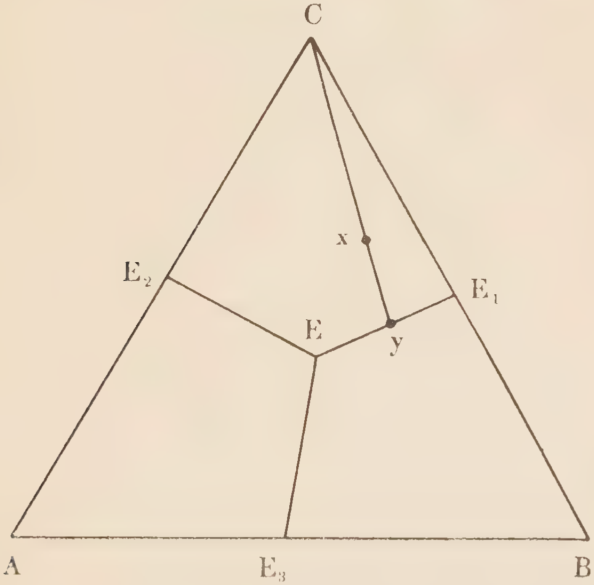

Fig. 26.—The course of crystallization in a simple ternary eutectiferous system.

while the third cannot form any solid solutions. Here one of the binary systems, say AB, will show the characteristic arrangement of liquidus and solidus curves as shown in Fig. 16, while the other pairs are eutectiferous as before. Here a complication is introduced by the fact that all crystals of the AB series show a crystallization interval instead of a true freezing point. However if the liquidus only is considered the matter becomes comparatively simple. Every plane vertical section through C can then be considered as a binary system of C and A_xB_y, the ratio $x:y$ being indefinitely variable along AB. But between every possible A_xB_y

and C there must be a possible eutectic showing the lowest freezing point along the line joining them. The eutectic ratio of C to A_xB_y will also be different for every A_xB_y mixture. Therefore there will be a gutter running obliquely across the diagram, which is often called the *eutectic limit*, or the *eutectic boundary*. Along this gutter only two surfaces meet and there is no definite ternary eutectic, only a continuous series of low-freezing mixtures along this line, as shown by the isotherms in Fig. 27. Such a case has been worked out in detail for the system diopside-plagioclase.

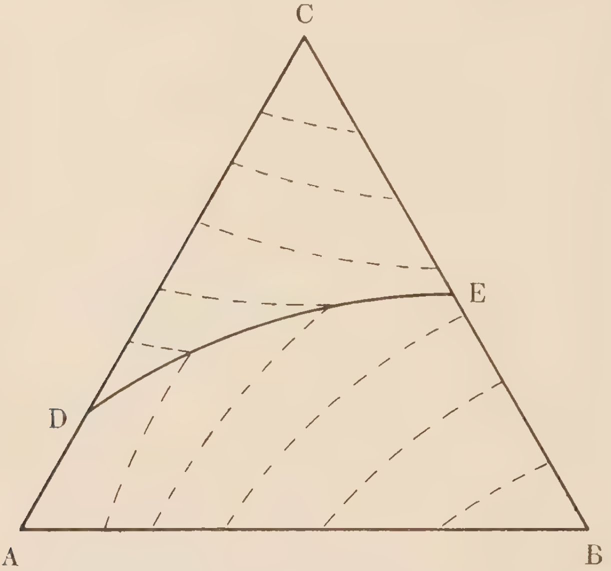

FIG. 27.—Form of liquidus surface, shown by isothermal contours, for the case where A and B show continuous solid solution, while C forms no solid solutions with either.

The course of crystallization in such a system is a little more difficult to visualize than in Case I since over part of the plane diagram there are in reality *two* surfaces, the liquidus and the solidus, converging at each end and at the eutectic boundary. Since A and B possess complete isomorphism the solid in equilibrium with the liquid represented by any point in the liquidus surface must contain a higher proportion of the higher freezing constituent (here assumed to be B). Therefore, starting with an indicating point x (Fig. 28) containing excess of C, at first this will travel as before along the line Cx. When it reaches the eutectic limit DE, a mixed crystal will begin to separate, whose composition is given by the point in the solidus surface at the same temperature as that of the liquid. This tie-line must of course be horizontal, and this implies that it must run obliquely back in the general direction of B. Further, in the binary system AB the continuous reaction principle applies, hence as y travels towards D, z will travel towards A, reacting with the liquid. The final result must of course be an aggregate of crystals of pure C and mixed crystals $AxBy$ whose bulk analysis is represented by the original point x, provided that equilibrium is established: that is to say it is a mixture of crystals of C and z'.

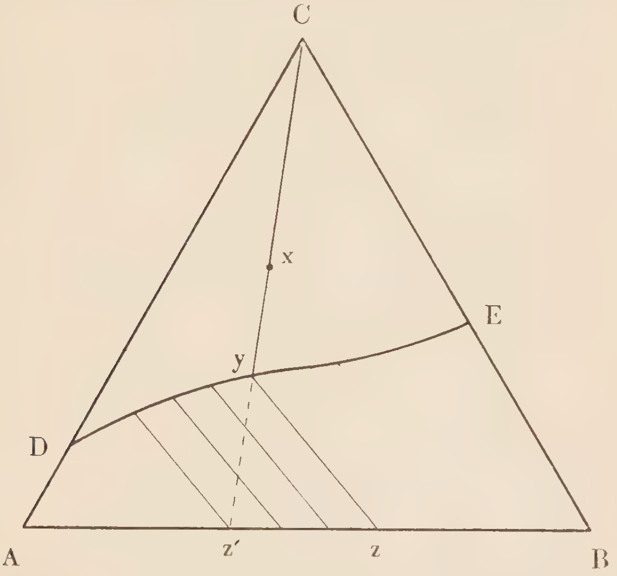

FIG. 28.—The course of crystallization in a system of the type shown in Fig. 27. Explanation in text.

Case III. One of the binary systems, AC, can form a molecular compound A_mC_n. Hence there must be a maximum along AC at the composition of the compound, and two eutectics. Consequently the liquidus surface will show a bulge with a gutter on either side. Each of these gutters will cut one of the other binary eutectic lines, giving rise to two ternary eutectics separated by a ridge. The course of crystallization will be clear from Fig. 29, in which arrows represent the directions of falling temperature and therefore also the slopes of the various segments of the surface. The fields of stability of A, B, C, and A_mC_n (or D) are also indicated. It is obvious that it is impossible for both pure *A* and pure *C* to separate from the same melt.

Case IV. A ternary compound *ABC* can be formed. This must be represented by some point within the triangle, and since a definite molecular compound always entails a maximum freezing point, whether on a line or on a surface, there must be a hump within the triangle, completely surrounded by gutters, as represented in Fig. 30. There are thus three binary eutectics and three ternary eutectics and a field of stability for *ABC* in contact with liquid limited on all sides. For the sake of simplicity binary compounds are here supposed to be excluded, although in nature this is very unlikely to happen.

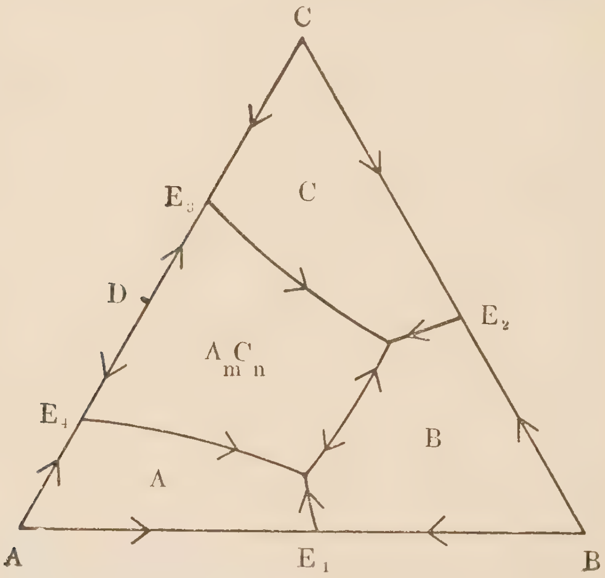

FIG. 29.—Eutectic diagram for the case where the components *A* and *C* form a molecular compound *D*, but there is no solid solution.

From what has already been said it must be clear that there are in ternary systems possibilities of endless complications, if we take into account such phenomena as partial miscibility, inversions with or without incongruent melting and so forth. In several systems that have been investigated in detail many of these complications are present: an excellent example is shown by the highly important system $CaO—Al_2O_3—SiO_2$, where two of the possible binary systems each show several intermolecular compounds and many of the products exist in two or more polymorphic forms, while there is at least one case of incongruent melting.

Multiple Systems. No attempt will here be made to discuss the phenomena observed in the solidification of systems of four or more components, although they are obviously of much geological importance, in reality more so than the simpler types. However they are too complicated for elementary treatment. A difficulty arises at the outset with regard to a method of graphic representation, since four co-ordinates are required. One system adopts as a basis the four equal edges of a tetrahedron, which are all equally inclined to each other, and another system employs a tetragonal pyramid. This method is often adopted in the representation of the equilibrium of double decompositions and reciprocal salt-pairs in solutions; this subject need not here be pursued on the theoretical side. Further references to complex systems of the kind indicated will be found in the chapter on metamorphism.

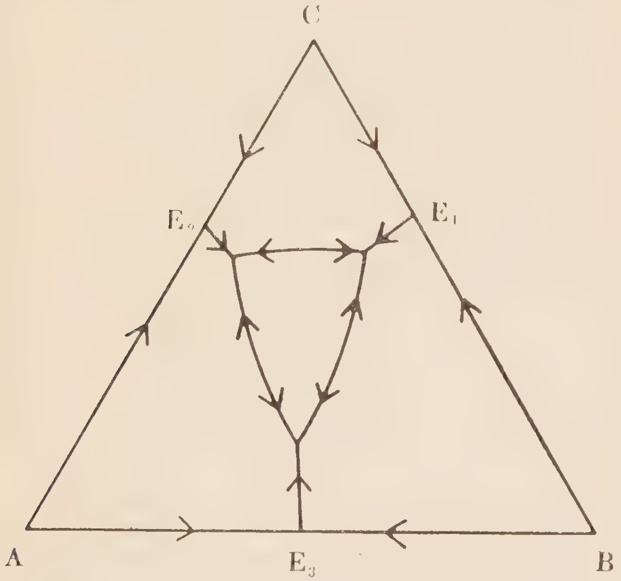

Fig. 30.—The Components *A*, *B* and *C* form a ternary compound, whose composition is given by some point within the inner triangle.

Attention must here be drawn to the fact that all the ternary types here described are condensed systems, the pressure variable being omitted, for the sake of simplicity. But it must always be remembered that pressure shifts all the points on these diagrams, both freezing points of simple components, freezing curves and surfaces of multiple systems and all types of eutectics. Within the range of pressures experimentally attainable the effects appear to be small, but in dynamic metamorphism there can be no doubt that this factor is of great importance : for example garnet is never obtained from artificial melts at atmospheric pressure, but it is one of the commonest minerals in high-pressure rocks. The field of stability of garnet is never touched by any of the freezing-point surfaces at atmospheric pressure in the lime-alumina-silica or magnesia-alumina-silica systems. We have to visualize the lines in the ternary diagram as being sections of surfaces, as a rule steeply inclined, and meeting and diverging at higher levels within the trigonal prism (produced upwards) of the solid model. Thus the region of stability of a given compound can be conceived as a solid in three dimensions, usually bounded by curved surfaces. Since the effect of pressure is merely to raise (or lower) freezing points no new co-ordinate is really required and the upper part of the model must be visualized as a triangular prism built up of all sorts of queer-shaped blocks, fitting closely together, each surface representing an equilibrium, and the space within each block the stability region of a compound relative to the other compounds with which it is in contact. The effects of diminished pressure hardly need consideration from the geological point of view, and the freezing-point surface at atmospheric pressure may be taken as the base of the structure here attempted to be described. The author does not feel competent to produce a single figure to illustrate this idea : it could be represented by serial sections which would take up too much space.

Systems with a Vapour-phase. Hitherto in dealing with systems of one or more components according to the principles of the phase-rule we have in most cases treated them as condensed systems, omitting the pressure variable and dealing with phenomena as occurring under the atmospheric pressure. Although of minor importance in geology and mineralogy, nevertheless there do exist a few cases of mineral formation by deposition from vapours, or by reactions between vapours : these are mostly connected with eruptive vulcanicity and its after-effects. At this point very brief mention may be made of the class of effects comprised under the general name of *pneumatolysis*, using the term in its widest sense, which is in fact an extension of its original meaning.[1] In the case of deep-seated pneumatolytic effects a difficulty is introduced by the fact that we do not know whether the substances involved in the processes are or are not above their critical points. Therefore it is necessary for the treatment of this subject to be mainly chemical rather than physical. There are, however, a number of natural operations that certainly go on under atmospheric pressure, involving a vapour phase, and some of these may here be considered briefly. From the geological point of view probably the most important of these is the condensation of the water vapour of the atmosphere to rain, or its freezing to snow, but a discussion of these hardly comes within the scope of this book. Further the important part played by water vapour in eruptive vulcanicity may be regarded as established, though of late years it has been questioned by at least one eminent authority.[1]

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[1] As originally introduced by Bunsen (1851) this term connoted very nearly what we now know as solfataric action in the less violent stages of vulcanicity.

The presence of gases, often of a highly complex character and with very active chemical properties, among the emanations of the later phases of volcanic activity and during periods of comparative quiescence in the history of spasmodically active volcanoes, is well known. This, which is commonly known as the solfataric stage, is described in all text-books and details need not be given. The point here is that by condensation of single gases, or by chemical reactions between the components of mixtures of gases, new minerals may be formed.

Sublimation. The formation of a solid mineral by condensation of a gas is often called sublimation, though this use of the term is hardly correct. The true nature of sublimation is most easily understood if we start with the solid phase. Now many solids possess measurable vapour pressure, and probably all solids in reality do so, though it may be immeasurably small at accessible temperatures. Thus the vapour pressure of ice at 0° is about 4 millimetres of mercury. The simple law here concerned is that if the vapour pressure of a solid in an open vessel at a given temperature is greater than the atmospheric pressure it will pass directly from the solid to the gaseous state, without melting. Since the vapour pressure of a solid is a function of the temperature it is clear that this variable has also to be considered. If now the vapour comes in contact with a cold surface it may be again condensed to a solid form, either crystalline or amorphous. This phenomenon takes place in many industrial processes, for example in the preparation of white arsenic from ores. The origin of the deposits of chlorides, especially ammonium chloride (sal-ammoniac) and ferric chloride, so common in and around the craters of volcanoes, is certainly to be explained in this way, and some sulphur deposits may originate by this simple type of sublimation. Similar effects are well known in blowpipe work and in various tests carried out by heating minerals in open or closed tubes. But a complication is often introduced by the possibility of dissociation on heating in the case of compounds: in such tests frequently the substance deposited is not the same as that originally introduced. The only perfectly clear case is that of "volatile" elements. Many apparent cases of sublimation are in reality nothing but distillation; the substance passing through a liquid phase, of which only a very small quantity is formed at any one time.

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[1] See Brun, *Recherches sur l'exhalaison volcanique*, Geneva, 1911. Summary in *Geol. Mag.* 1911, pp. 268 and 311.

The geological significance of this subject of course lies in the inverse process, the deposition of minerals directly from vapours: and this can rarely be observed directly owing to the uncomfortable or dangerous conditions that usually prevail while it is in operation; hence it is often uncertain whether such deposits are really formed by true sublimation, or by double decompositions, such as the well-known reaction by which sulphur can be formed:

$$SO_2 + 2H_2S = 2H_2O + 3S$$

Dissociation and its converse are undoubtedly important factors in such yrocesses.

The fact that ice possesses an appreciable vapour pressure has important practical consequences in that a considerable amount of ice or snow actually disappears by sublimation without melting. It is often noticeable even in this country that during a long cold spell with snow on the ground a good deal of the snow disappears, although what remains is quite dry and powdery. In regions with a more or less permanent covering of winter snow and in Arctic climates this must be quite an important factor in reducing the volume of snow and ice and thus diminishing the amount of water to be disposed of in thaws. The gradual disappearance of snow in England was very noticeable during the long cold winter of 1894–5, when the country was frost-bound for many weeks.

Aqueous Solutions. By the term solution the ordinary person commonly understands a homogeneous mixture of water and some other substance. In reality there is no essential difference between a solution in water and any other binary system in which there is a single homogeneous liquid phase, but in geology watery solutions play such an important part that a special and detailed consideration is necessary.

Most substances are soluble to some extent in water, but many mineral compounds only to a very slight degree. There appears to be no general law controlling the solubility or otherwise of different classes of compounds, and many closely allied substances behave very differently in this respect. Thus most chlorides and nitrates are very soluble, but the chlorides of silver, lead and mercury are not. Sulphates vary very much in this respect, while most sulphides except those of the alkali metals are insoluble. The same applies broadly to carbonates. Considering now the basic element in salts, nearly all compounds of the alkali metals are soluble, while in other groups of metals most of the salts are insoluble. Still all metals appear to form one or more soluble compounds: the whole thing seems to be quite arbitrary and a matter of chance. Again, in most cases solubility is increased by rise of temperature, but there are numerous exceptions. Solution in water is always accompanied by some thermal effect, either absorption or evolution of heat, so that the heat of solution measured in calories may be either positive or negative. Solution may also entail a decided change of total volume, the final volume being either greater or less than the sum of the initial volumes of the components.

Change of pressure also alters solubility, and here there is a definite law: when solution is accompanied by contraction of volume, solubility is increased by pressure, and vice versa. This is a simple application of Le Chatelier's principle. In practice, however, at attainable pressures the effect is not very great and can usually be neglected, or in other words, solutions can generally be treated as condensed systems. This of course does not apply to solutions of gases in liquids, where pressure is all-important: we are now, however, considering only solutions of solids in liquids.

As already stated in the first chapter an unsaturated solution is to be regarded as a system in homogeneous equilibrium and hence not of much interest, but a saturated solution in contact with solid is a binary system in heterogeneous equilibrium, according to the terminology of the Phase Rule a bivariant system, since

$$f = 2 - 2 + 2 = 2.$$

It has been agreed to eliminate pressure as a variable for the present, therefore as a condensed system a saturated solution is univariant. In plain language this is only another form of the statement that solubility is a function of temperature. From the data obtained by experiment it is therefore possible to construct curves by plotting solubility, or the amount of solid dissolved in a given mass of water, against temperature.

Solubility curves as thus obtained show very wide variations of form: if the solubility of a substance increases rapidly with a rise in temperature the curve may be very steep: if the solubility is nearly constant it may be an almost horizontal line: it may be either straight or curved, and in certain cases, to be discussed presently, the curve may be discontinuous, with a sharp bend or even a reversal of direction. A few forms of curves characteristic of substances of geological interest are shown, not drawn to scale, in Fig. 31. Some points of much interest concerning the solubility of calcium sulphate are dealt with in Chapter IX.

The Solubility of Common Salt. Since sodium chloride is perhaps the most abundant soluble salt found in nature, its solubility relations are of some interest. In the first place the solubility increases only very slightly with rise of temperature, hence the temperature-solubility curve is a nearly horizontal straight line. Hence rock salt will be deposited from a saturated solution, say a salt lake, into which salt is continually being carried by rivers, at nearly the same rate in winter and summer, always provided that the supply is constant.

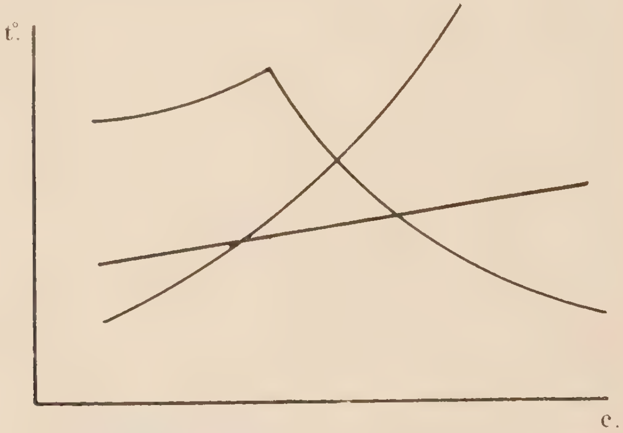

Fig. 31.—Typical forms of solubility curves, not drawn to scale, and not representing any particular salts.

The next point to be considered is the influence of the salt on the freezing point of the water. According to the universal law, addition of salt lowers the freezing point of the water, at a rate nearly proportional to the amount of salt added. Hence if the curves representing the solubility of the salt and the freezing point of the water in the solution are plotted on the same *ct* diagram, they will intersect at a point (Fig. 32). This point, which lies at — 22° C. and 23·6 per cent. of salt, represents the lowest temperature possible in the liquid, and is therefore the lowest temperature that can be obtained by mixing ice and salt. In other words, if 23·6 per cent. of salt and 76·4 per cent. of ice are intimately mixed together the temperature of the mass will fall to — 22°. It was once supposed that this mixture corresponded to a definite compound of NaCl and H_2O, and it was called a cryohydrate.[1] In reality, however, there is no chemical combination and this so-called cryohydrate is precisely similar to the eutectic as defined on p. 26. It is the mixture of salt and water having the lowest possible freezing point, and will freeze at constant temperature, the resulting solid being an aggregate of crystals of salt and crystals of ice. Since natural fresh water is never perfectly pure, but always contains dissolved salts, natural ice, including even glacier ice, consists of crystals of pure ice separated by thin films of lower-freezing-point mixtures; hence such ice on the approach of a thaw will tend to break up into loose crystals separated by films of liquid, even before the air temperature has risen to 0°, and it is of course specially liable to occur with ice formed at a very low temperature. This fact accounts for many skating accidents. Since sea-water contains over 3 per cent. of dissolved salts, largely sodium chloride, its freezing point is naturally several degrees lower than that of fresh water.

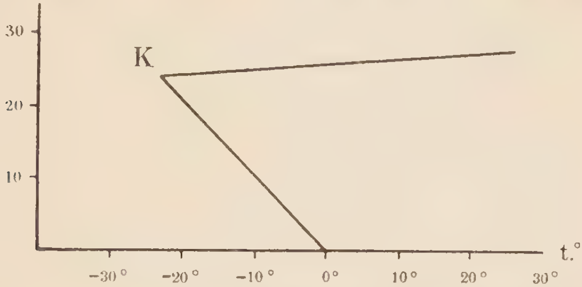

Fig. 32.—The cryohydric (eutectic) point for water and NaCl.

The nearly horizontal line is the solubility curve of NaCl: the steeply inclined line the freezing-point curve for mixtures of NaCl and water. *K* is the cryohydric point:—22° C. and 23·6 per cent. NaCl.

The Solubility of Salt Hydrates. Many soluble salts have the property of forming definite crystalline compounds with a fixed quantity of water, known as water of crystallization. In some cases the simple anhydrous salt also exists as a mineral. Thus gypsum is $CaSO_4.2H_2O$ while anhydrite is $CaSO_4$. These two substances crystallize in different systems and have altogether different physical properties in the solid state. The existence of the salt in the hydrated and anhydrous forms respectively, depends mainly on the temperature. Thus from a solution of calcium sulphate gypsum separates at temperatures below about 60°, anhydrite above this. This temperature of 60° is therefore called the inversion point for gypsum and anhydrite. It is often found that the solubility curve undergoes an abrupt change of direction at an inversion point and may even be reversed. This is well known in the case of Glauber's Salt, sodium sulphate. At low temperatures the form stable in contact with solution is the decahydrate, $Na_2SO_4.10H_2O$: the solubility of this increases with rise of temperature up to 32·6° C. At this point the solid changes to the anhydrous salt, Na_2SO_4, and the solubility of this decreases as the temperature rises further. Under special conditions another form, $Na_2SO_4.7H_2O$, can be obtained ; this is always unstable with respect to the decahydrate. At high pressures still further complications occur, but these need not be considered here.[1]

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[1] Guthrie, *Phil. Mag.*, Ser. 4, vol. xlix, 1875, p. 1.

Some further points connected with the solubility of calcium sulphate will be dealt with in Chapter IX, under the heading of salt deposits, where also some other noteworthy examples of salt hydrates will be discussed.

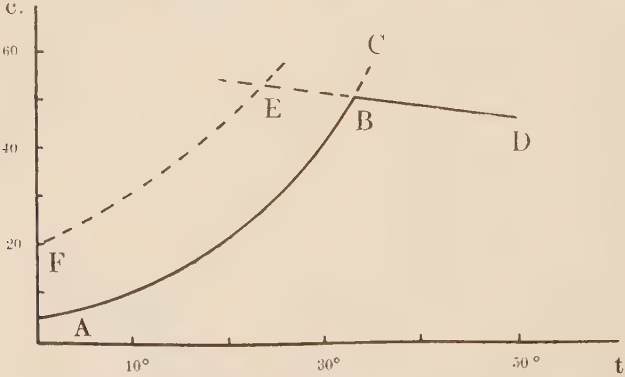

FIG. 33.—The solubility curves for sodium sulphate.

AB = solubility of $Na_2SO_4.10H_2O$; *BD* = solubility of Na_2SO_4 ; *FE* = solubility of $Na_2SO_4.7H_2O$.

Mixed Salt Solutions. The effects produced by the mixing of salt solutions are very varied, and of much geological importance, since they undoubtedly lead to the direct deposition of many minerals. In studying this subject it must always be remembered that natural solutions, especially those found underground, are as a rule extremely dilute, so that their effects are not exactly analogous to those brought about by the comparatively strong and often saturated solutions used in the laboratory and in industrial processes. This point is well shown by the first case to be considered.

Perhaps the simplest type is that afforded by the very common instance that two solutions that are mixed contain compounds, themselves separately soluble, but capable of forming an insoluble compound on mixing. In such a case the insoluble compound always appears as a precipitate. Instances are almost too numerous to mention: specific examples will crop up later; e.g. formation of barytes, horn silver, copper carbonates.

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[1] For full details see Wuite, *Zeits. phys. Chem.*, vol. lxxxvi, 1914, p. 349.

Since such natural solutions are generally extremely dilute they must be almost completely ionized, but the really important point connected with the high degree of dilution is this. When in laboratory tests a fairly strong solution of, say, barium chloride is mixed with a soluble sulphate there at once comes down a voluminous precipitate of barium sulphate, which appears to be entirely amorphous. But the mineral barytes, having the same composition as the precipitate, is found as very large and well-developed simple crystals, up to several inches in length, embedded in clays, where they must have grown by precipitation from solutions. The explanation is that the barytes, which is to a very minute extent soluble in water, was formed by extremely dilute solutions, which precipitated the salt, perhaps one molecule at a time, or at any rate, very slowly, close to a nucleus of crystallization. The very minute amount formed was sufficient just to supersaturate the solution and the nucleus then caused its precipitation as part of a regular crystal structure. The common occurrence in nature of large and well-formed crystals of very insoluble substances can only be explained in some such way. The time factor is all-important.

It is unnecessary to pursue any further at this point the important subject of mineral formation by double decomposition. The conditions of equilibrium are somewhat complicated, but the practical effect is that the mixing of two solutions produces a system of a solid and a liquid phase, the concentration of the salts dissolved in the liquid being very small. There must be at least four components, so that the system is divariant, and therefore capable of existing within a considerable range of temperature and pressure. One limit is given by the possibility that at higher temperatures and pressures the precipitate may be completely soluble in the liquid phase: in other instances it may be less soluble, so that precipitation may be more complete from hot solutions. Here again there is always the possibility of solid inversions, so that the final product may be different at different temperatures.

The crystallization of mixed salt solutions is an extraordinarily complicated subject and to discuss even the main principles fully would require a large book to itself, as may be seen by a glance at Van't Hoff's work on the oceanic salt deposits.[1] Nothing of the sort can be attempted here, but only one or two points of general interest will be very briefly mentioned.

[1] Van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, 1905.

In the study of the behaviour of mixed salt solutions two points are of special interest and importance: (1) the effects of one salt on the solubility of other salts, and (2) the formation of double or more complex salts.

With regard to the first point, the general rule is that the addition of a second salt to a solution diminishes the solubility of the first salt, and it has been found that this effect is specially well marked if the two salts contain a common ion. This has been enunciated by Nernst as a general law, and is known as Nernst's Law of the Common Ion. It applies equally to the acid and to the basic radicles in the salts. Thus a chloride will greatly diminish the solubility of a chloride, while two salts of the same metal have a similar effect. As a further example of the general principle, hydrochloric acid will cause a nearly complete precipitation of sodium chloride from a saturated solution of common salt.

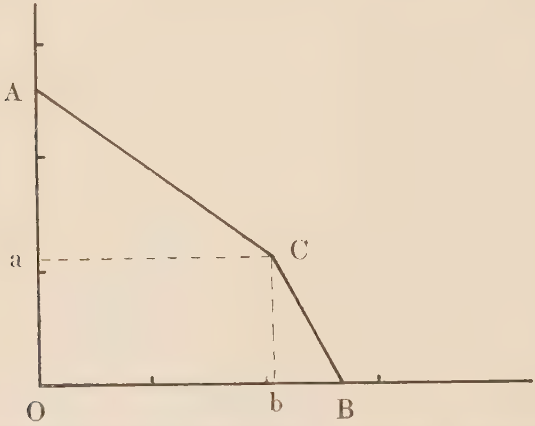

FIG. 34.—Solubility curve for binary salt mixtures at a given temperature: at *C* the system is saturated for both salts.

A solution of two salts in contact with both solids is in reality a three-component system, but can be represented by a diagram constructed on two rectangular axes, as in Fig. 34. In this diagram the co-ordinates represent the solubility of each salt in a given mass of water, *A* and *B* being the solubilities of each salt alone. The temperature must be assumed to be constant; the figure is in reality an isothermal section of a three-dimensional model of a condensed system, pressure being ignored. Since the addition of *B* lowers the solubility of *A*, and vice versa, two curves are obtained which must eventually intersect at a point within the diagram, *C*. This indicates a solution saturated with respect to both *A* and *B*, and has a close analogy to a eutectic point. The saturated solution and the mixed salt that separates from it on isothermal evaporation at this temperature will contain the mixed salts in the ratio $Oa : Ob$, provided no double salt is formed. Since the ratio of the two salts in the doubly saturated mixture varies with the temperature, it is obvious that this saturation point cannot correspond to the composition of a double salt. If temperature is taken into account along a third rectangular co-ordinate we shall obtain two solubility surfaces intersecting in a line which may be called a *line of double saturation.*

An interesting example of the application of this principle of diminished solubility will be found in a later chapter in connection with deposition of salts from certain lakes.

Double Salts. The study of the behaviour of natural salt solutions under varying conditions is immensely complicated by the formation of numerous double and even triple salts, as well as by the occurrence of different hydrates of the same salt. The investigation of these relations is, however, of special importance in connection with the commercial separation of potash salts for industrial purposes on the large scale. The formation of double salts from aqueous solutions is essentially of the same nature as the formation of molecular compounds in binary systems: with this important exception, namely that in dilute solution double salts appear to be completely dissociated into the same ions as the single salts. The depression of the freezing point produced by a double salt, for example, is equal to the sum of the depressions due to the two single salts. But in concentrated solutions combination appears to persist to some extent. As a rule double salts are less soluble in water than the components. This follows from what has been said above as to lowering of solubilities.

As a rule both the components of a double salt possess some element in common, either in the acid or the base, e.g. carnallite, $KCl.MgCl_2.6H_2O$, or schoenite, $K_2SO_4.MgSO_4.6H_2O$, both found in the Stassfurt salt deposits. A very unusual type of double salt from the same locality is kainite, $KCl.MgSO_4.3H_2O$: in this the two components have nothing in common.

Salt Hydrates. As before stated many salts have the property of crystallizing with several different proportions of water, the general rule being that the higher degree of hydration is stable at lower temperatures. For example, magnesium chloride forms five different hydrates, with $12H_2O$, $8H_2O$, $6H_2O$, $4H_2O$ and $2H_2O$ respectively: when a saturated solution of magnesium chloride is gradually heated the solid salt in contact with the liquid progressively changes from the higher to the lower hydrates in the order stated, giving rise to discontinuities in the solubility curve : the analogous phenomena shown by the hydrates of ferric chloride are discussed in every textbook of physical chemistry. The changes in solubility of the sulphates of sodium and calcium are due to a similar hydration or dehydration of the solid salt in contact with the solution.

Some very peculiar effects are seen in connection with the water of crystallization of the minerals of the zeolite group. Although these are definitely crystalline minerals, nevertheless the water of crystallization is held so loosely that it can be driven off by a continuous process, without any apparent change in the structure of the crystals, which remain quite clear and transparent. In fact the amount of water in the crystal is solely a function of the temperature : the most reasonable explanation is to regard the zeolites as solid solutions of water in silicates. There is a close analogy between their behaviour and that of certain amorphous hydrated compounds, such as ferric hydrates and aluminium hydrates. Measurements of the vapour pressure of such amorphous hydrates and of zeolites during the dehydration show a continuous curve, whereas the vapour pressure of such a salt as magnesium chloride on heating shows a series of steps, each corresponding to the definite loss of a fixed number of molecules of water of crystallization and a change in the appearance of the salt : thus $CuSO_4.5H_2O$, is blue, but $CuSO_4.H_2O$ is colourless. The dehydration of the zeolites is a completely reversible process.

Very different is the behaviour of certain other silicates, e.g. mica, which also contain the elements of water, but only give it off at very high temperatures, often at a red heat. This is called water of constitution, but probably does not exist as such in the mineral ; the hydrogen being probably combined as OH and not as H_2O. In some instances both appear to be present, as part of the water is given off at a low temperature and part only on strong heating.

The constitution of colloidal sols and gels is dealt with in a separate chapter.

To sum up the main facts of geological importance discussed in this section : a mixture of two solutions often causes precipitation of solid minerals ; the more salts there are present in a solution the less is the solubility of each individual salt, especially in the presence of a common ion ; inversions in the solid salt and the formation of hydrates often cause great complications in the separation of salts from saturated solutions, such as salt lakes ; water is held by minerals in several essentially different ways ; all of these are of importance in the formation of both igneous and aqueous rocks.

CHAPTER III

ISOMORPHISM AND SOLID SOLUTION

Mixed Crystals. Very few natural minerals yield on analysis an absolutely pure chemical compound : there is nearly always an admixture in varying proportions of other substances, sometimes as mere traces, sometimes in amounts so large that the mineral has to be regarded as a mixture of two or more principal molecules. In innumerable instances the characteristic colours of minerals are actually due to the presence of some impurity, which can only in reality be considered as accidental. A good example is afforded by the varying colours of many gem-stones.

There are here two different classes of phenomena to be considered ; namely, in one case the impurity consists of a mechanical admixture of some other substance in the solid form, either crystalline or amorphous. These may be classified as inclusions. In the other case the second substance forms a perfectly homogeneous mixture with the first and must be regarded as forming an integral part of the mineral. This is the type to be dealt with here. The subject of inclusions cannot, however, be wholly excluded, since, as will be seen later, there is reason to believe that some at any rate have separated from a state of homogeneous mixture after the mineral became solid. This effect is well known to occur in many metallic alloys, and indeed metallography in general has thrown much light on the subjects discussed in this chapter.

For the present attention will be confined to those instances where on optical examination the minerals appear to be homogeneous. This principle is of first-class importance in geology and mineralogy, whether pure or applied, since the majority of the common rock-forming minerals of the igneous rocks, and a very large number of the ore-minerals and of the so-called non-metallic minerals belong to this category. The fundamental idea can be most easily explained by an actual example. For instance analysis of an apparently pure and homogeneous crystal of olivine might show that it contained MgO, 37·14 per cent. ; FeO, 22·60 per cent. ;

CaO, 1·95 per cent. ; and SiO_2, 38·31 per cent. When these figures are treated in the usual manner, namely, division by the molecular weights of each compound, the results are as shown below.

$$\begin{array}{llll} & \text{per cent.} \quad \text{mol. wt.} & & \text{Mol. ratios.} \\ \text{MgO} \quad . \quad . \quad . & 37{\cdot}14 \div 40 = {\cdot}9285 & \multirow{3}{*}{$\left.\begin{array}{l} \\ \\ \\ \end{array}\right\}$} & \\ \text{FeO} \quad . \quad . \quad . & 22{\cdot}60 \div 72 = {\cdot}3139 & & = 1{\cdot}2772 = 2 \\ \text{CaO} \quad . \quad . \quad . & 1{\cdot}95 \div 56 = {\cdot}0348 & & \\ SiO_2 \quad . \quad . \quad . & 38{\cdot}31 \div 60 = {\cdot}6385 & & = \quad {\cdot}6385 = 1 \end{array}$$

The molecular ratios are then grouped in accordance with the chemical affinities of the constituents : in this instance as all the basic oxides are divalent they are added together, giving the sum 1·2772, which is almost exactly double the amount of silica found by the same process ; hence it is clear that the mineral contains basic and acid radicles in the ratio of 2 : 1, and is therefore an orthosilicate, which can be written as $2R''O.SiO_2$, or R''_2SiO_4.

The next problem is to find in what proportion the three different orthosilicates of magnesia, iron and lime are present in the mixture. For this purpose we proceed as follows :

Taking as an example the calculation of the percentage of Mg_2SiO_4 present in the mixture, we proceed as follows :

$$\begin{aligned} Mg_2SiO_4 &= 2\ MgO + SiO_2 \\ &= 2(24 + 16) + \{28 + (2 \times 16)\} \\ &= 140 \\ MgO &= 40 \text{ or } 2\ MgO = 80 \end{aligned}$$

Hence the percentage of MgO in the analysis must be multiplied by $\frac{140}{80}$, and similarly for the other basic oxides present.

$$\begin{aligned} & & &\text{Per cent.} \\ 37{\cdot}14 &\times \frac{140}{80} &= &\ 65\ Mg_2SiO_4 \\ 22{\cdot}60 &\times \frac{204}{144} &= &\ 32\ Fe_2SiO_4 \\ 1{\cdot}95 &\times \frac{172}{112} &= &\ \ 3\ Ca_2SiO_4 \\ & & &\overline{\underline{\underline{100}}} \end{aligned}$$

Thus the molecular formula of the mineral can be written as

$$65\ Mg_2SiO_4.32\ Fe_2SiO_4.3\ Ca_2SiO_4.$$

It is thus a ternary mixture and its composition can also be represented graphically on a triangular diagram, as explained in Chapter II. The principle here employed can be used in dealing with all analyses of mixed minerals of this type.

With regard to the method of grouping the different oxides shown in the analysis, it is possible to draw up a very simple rule, applicable in the majority of instances. *The oxides of elements having similar valencies are grouped together.* This rule works very well for example in the case of the rock-forming silicates. Here the principal oxides are silica, alumina, ferrous and ferric oxides, magnesia, lime, potash, soda and water ; with in smaller amounts titania, manganese oxides, chromium oxides, barium and strontium oxides, lithia and others. According to their valencies these can be arranged in groups, as follows :

Tetravalent . .	SiO_2, TiO_2
Trivalent . . .	Al_2O_3, Fe_2O_3, Cr_2O_3
Divalent . . .	MgO, FeO, CaO, MnO, BaO, SrO
Monovalent . .	K_2O, Na_2O, Li_2O, H_2O

Many of the heavy metals, copper, lead, zinc, nickel, cobalt, etc., also occur in traces and fall into their proper places in the scheme.

Of these groups, the first, containing silica, is pre-eminently that of the acid-forming oxides. In some cases titanium apparently replaces silicon in small quantities. In the spinel group and in some other non-siliceous minerals the trivalent oxides seem to play the part of an acid radical, while they can exist alone as stable minerals, in corundum, hæmatite, etc. The divalent and monovalent oxides are always basic and do not exist as minerals, except MgO (periclase). Water is as usual exceptional in its behaviour. Many of the silicates containing alumina and other bases are commonly regarded as salts of alumino-silicic acids of complex composition : here again the acid radical is compounded of the first two groups. Here are included such important mineral families as the felspars, felspathoids, zeolites and the scapolite group. The micas and garnets require a little further consideration before they can be assigned to this category, although at first sight there seems to be much affinity. The family of the carbonates is also of much interest from this point of view.

The formation of crystals of mixed composition, as here briefly outlined, has been commonly called *isomorphism.* For such products the term *mixed crystals* is often used, but it is not very appropriate, since it fails to bring out clearly the fundamentally important fact that such mixtures are homogeneous. It might just as well be employed for cases of mechanical inclusions. As will appear shortly there is actually a very close analogy with liquid solutions, which are defined as homogeneous mixtures of two components. This definition implies nothing as to the state of aggregation of the system, and it was suggested by Van't Hoff that the term *solid solution* should be employed ; this usage is now universally accepted, and it must be clearly understood that the terms isomorphous mixture, mixed crystal and solid solution are in reality synonymous. From this point of view such amorphous aggregates as the silicate and borate glasses must also be included, since these are now regarded as undercooled liquids of very high viscosity. For the present, however, only crystalline solid solutions need be considered.

It may perhaps profitably be pointed out here that the meaning of the term isomorphism is in reality somewhat vague, since it has been used in several different senses. The original meaning as put forward by Mitscherlich in 1821 was that two or more substances of analogous chemical composition possessed an identical or closely similar crystal form : that is, the term was strictly confined to *form*. Later it was observed that certain groups of elements could form various series of analogous compounds, and these groups were also spoken of as isomorphous. Subsequently the idea got mixed up to a considerable extent with the periodic law of Mendeléev, and chemists spoke of isomorphous elements, without taking into account whether there was any particular relationship in the crystal forms of these elements ; this is an incorrect application of the original term, which should be restricted to cases where crystal-forms and other physical properties are closely related. In the original definition the capacity to form mixed crystals was not implied, but the term is now commonly understood in that sense.

The Physical Chemistry of Solid Solutions. It has already been stated that a very close analogy exists between solid and liquid solutions, and this can now be carried further. In the first place it is to be remarked that the mutual miscibility in the solid state is not always unlimited. Just as some liquids will mix in any proportion, e.g. water and alcohol, so will some solids, like the silicates of magnesium and iron, as before described. On the other hand, some liquids have a definitely limited miscibility, like water and phenol, while others will not mix at all, like water and oil. There are analogues of both these conditions also in solids. Further, experiment shows that just as with partially miscible liquids so with many solids, the degree of miscibility is a function of the temperature and pressure.

In any physico-chemical treatment of this subject the one fundamental fact is that in true solid solutions the physical properties are continuous functions of the temperature and pressure: this is equivalent to saying that solid solution is controlled by the same thermodynamic laws as liquid solution. Here also, just as in the study of aqueous solution, it is important to get rid of any preconceived ideas as to a distinction between solute and solvent. A solution of any kind, whether gaseous, liquid, or solid must be regarded simply as a homogeneous mixture of two or more substances capable of independent existence. A solid solution therefore must always be at least a binary system in one phase and hence possessing two degrees of freedom, which means that temperature and pressure can be varied independently (within limits) without any necessary change in the number of phases. Many solid solutions possess a very wide range of stability, and it is possible for the system to pass through an inversion point without loss of homogeneity, although there must then be some energy change, as shown by a thermal effect.

The phenomena attending the freezing and melting of solid solutions have already been described in Chapter II, and need not be again discussed here. It was shown that in such a system the solid and liquid in equilibrium at a given temperature have different compositions, and consequently the freezing and melting of a particular mixture begin at different temperatures, giving rise to a crystallization interval. Hence the cooling curve of any member of a completely isomorphous series shows no horizontal arrest, but only two changes of slope, one at the beginning and one at the end of the crystallization interval. With limited miscibility the cooling curves are more complex, and this statement does not in general apply, since between the limits of solid solubility a eutectic can exist, and mixtures between these limits will show a eutectic arrest (see p. 34).

It has already been shown that in the crystallization curves of completely isomorphous mixtures three types are possible: in the most common case the curves for liquid and solid lie wholly between the freezing points of the two components (see Fig. 15). Of this type the plagioclase felspars form an admirable example. The type of curve with a maximum is not known to exist among minerals, while the form with a minimum is believed to be rare, but one good example has been described in the case of the åkermanite-gehlenite series.[1] Åkermanite is in fact only known in artificial melts and has the composition $2CaO.MgO.SiO_2$, while gehlenite, $2CaO.Al_2O_3.SiO_2$, is known as a rare mineral. Although these two formulæ are not strictly analogous it is found that isomorphous mixtures exist, the physical properties of the solid solutions being continuous functions of the composition: these crystals appear to be identical with some natural forms of melilite. The liquidus-solidus curves have been determined with great care: a minimum is clearly established at 1,388°, with 74 per cent. åkermanite and 26 per cent. gehlenite. The forms of the curves are shown to scale in Fig. 35. The complete study of the åkermanite-melilite-gehlenite series is of the greatest importance in the investigation of blast-furnace slags, in which they are extremely common: in fact melilite in the broad sense may be said to be the characteristic constituent of modern slags from furnaces of a high grade of efficiency. It will be noticed that on the gehlenite side of the diagram the crystallization interval is as much as 70° at about 40 per cent. gehlenite. This wide difference between the temperatures of the beginning of freezing and the beginning of melting is a point of considerable practical importance. Some uncertainty at one time existed and probably still exists as to the exact composition of åkermanite and gehlenite: in many books of reference different molecular formulæ will be found, but the ratios here given correspond to the latest results available.

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[1] Ferguson and Buddington, *Amer. Jour. Sci.*, vol. 1, 1920, p. 131.

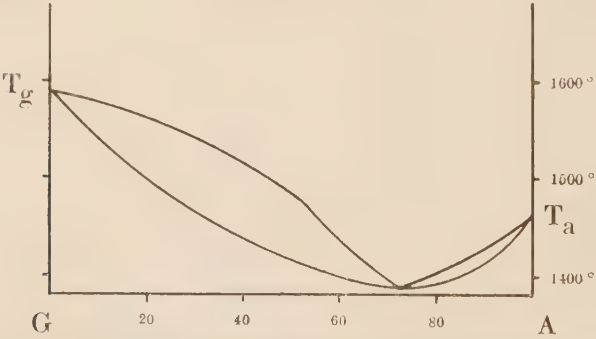

Fig. 35.—Freezing and melting curves for the system gehlenite—åkermanite.

(After Ferguson and Buddington, *Amer. Jour. Sci.*, vol. 1, 1920, p. 133.) Continuous solid solution, the curves passing through a minimum.

Turning now to certain points of theoretical interest to be derived from this diagram, it is to be noted in the first place that at a given temperature there may be two pairs of liquids and solids in equilibrium, having entirely different compositions, but above the freezing point of the lower-freezing component there can be only one pair. The general course of crystallization on such a curve-system is exactly the same as in the first case mentioned, the principle of continuous reaction applying equally in this instance, while zonary crystals are equally possible and are indeed commonly observed in the melilite series. The minimum point at 1,388° and 74 per cent. Åk has some of the properties of a eutectic, but the lower curve is continuous throughout and its tangent at the minimum must be horizontal, whereas in a eutectic system there is no common tangent at the point of intersection, the two curves meeting at an angle.

In the case just described it is evident that the addition of one component lowers the freezing point of the other, as usual, but it is to be noted that in the other two cases the freezing point of one or both the components is *raised* by the addition. This possibility must be regarded as characteristic of solid solutions, as opposed to eutectiferous systems.

Isomorphism. The physical phenomena accompanying isomorphism in general have been very extensively studied by crystallographers, in connection with both artificial salts and natural minerals. It is impossible here to deal fully with this interesting subject, but one or two special points may be briefly mentioned. Detailed investigations have been carried out for the most part on pure compounds of related type rather than on mixed crystals; the chief results of much work on this subject have been summed up by Tutton as follows:[1] "The whole of the properties, morphological and physical, of the crystals of an isomorphous series are functions of the atomic weights and atomic numbers of the interchangeable chemical elements of the same family group which give rise to the series." By the methods of X-ray analysis it has even been found possible to demonstrate a simple relationship in the dimensions of the structural units of which such crystals are built up. This subject however belongs to mineralogy rather than to geology, and cannot here be pursued further. For our present purpose the study of mixed crystals is of greater importance, and some actual examples will now be considered.

The Garnet Group. Perhaps the most striking case known to us of isomorphism in the widest sense of the term is that of the garnet group. Here we have a large number of minerals, or mineral varieties, all showing identically the same crystal-symmetry (cubic) and for the most part the same crystal-faces. Within this group there is a wide variation of chemical composition and most if not all garnets are undoubtedly mixed crystals (solid solutions). This is all the more striking in that the chemical composition is somewhat complicated, the simplest possible representation of the formula being as a double silicate. Further, in the garnet group a large number of elements are capable of replacing each other. There is also every reason to believe that in some members of the group at any rate the solid solubility is limited.

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[1] Tutton, *Natural History of Crystals*, London, 1924, p. 103.

If we represent as usual a divalent metal by R″ and a trivalent metal by R‴, the general formula of the garnet group is

$$3R''O.R_2'''O_3.3SiO_2$$

which works out as an orthosilicate. The chief metals present in the divalent molecule are Ca, Mg, Fe″, Mn; in the trivalent group Al, Fe‴, and Cr. Titanium is found in many garnets; its relations will be discussed later.

This series affords a good opportunity of introducing a new term, of wide application in the study of mixed crystals. When a series of elements are capable of replacing each other in such minerals, they are said to be *vicarious*. Thus in the garnet group there are two vicarious series, divalent and trivalent respectively.

The following list includes the more important varieties of garnet as generally recognized by mineralogists: innumerable unnecessary names have been applied to varieties of little importance:

Grossularite	$3\,CaO.\ Al_2O_3.\ 3\,SiO_2$
Pyrope	$3\,MgO.\ Al_2O_3.\ 3\,SiO_2$
Almandine	$3\,FeO.\ Al_2O_3.\ 3\,SiO_2$
Spessartite	$3\,MnO.\ Al_2O_3.\ 3\,SiO_2$
Andradite Melanite	$3\,CaO.\ Fe_2O_3.\ 3\,SiO_2$
Uvarovite	$3\,CaO.\ Cr_2O_3.\ 3\,SiO_2$

The above are generally recognized types, but it must be understood that they have no real existence as definite mineral species. All garnets are solid solutions, approximating more or less to the above types, since in some instances the solid solubility appears to be limited. According to a careful revision by Boeke[1] of a very large number of published analyses of garnets, it is clear that in the aluminous group complete mixed-crystal series exist between pyrope and almandine and between almandine and spessartite, whereas pyrope and spessartite are miscible in a very limited degree, if at all: in other words the pairs of oxides MgO–FeO and FeO–MnO are completely vicarious, whereas MgO and MnO will not mix to any large extent. Again alumina and ferric oxide appear to be completely replaceable in the lime-garnet series, whereas garnets with MgO, FeO or MnO, and Fe_2O_3 are not known. Fig. 36, somewhat modified from Boeke, shows the extent to which the composition of alumina garnets can vary. The general conclusion to be drawn from these facts is that MgO, FeO and MnO form a mutually replaceable group, whereas CaO is on the whole antithetical to them, but on the other hand lime alone can form a ferric-iron garnet (andradite or melanite).

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[1] Boeke, *Zeits. für Krist.*, vol. liii, 1913, p. 149.

If we consider the miscibility of the $CaO-Al_2O_3$ garnet molecule with the $(Mg, Fe, Mn)O-Al_2O_3$ garnet molecule, we find an immiscibility interval between about 20 and 75 per cent. of the last named. Unfortunately it is not possible to test all this by means of the usual melting-point and freezing-point determinations, since garnet cannot be made artificially from dry melts, and when heated melts incongruently, to a number of different minerals and liquids. If any natural garnet is melted and cooled it crystallizes as a mixture of anorthite, melilite, hæmatite, etc., according to the variety used. Hitherto only a very few examples of artificial garnets, made with the help of a flux, are on record.

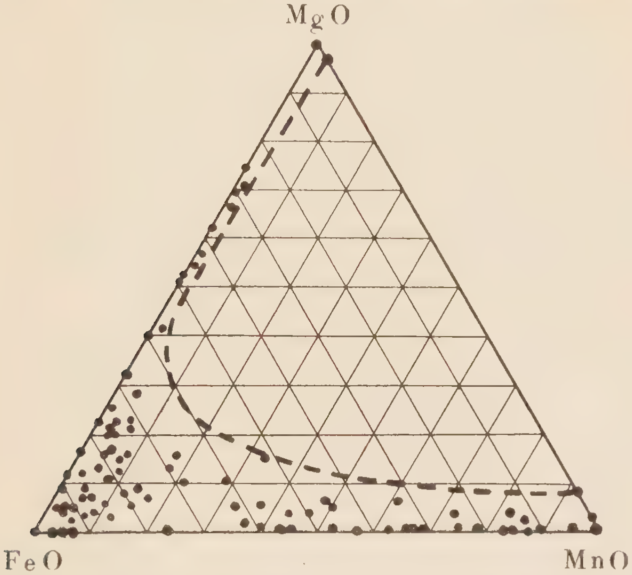

Fig. 36.—The composition of the garnets free from lime.

(After Boeke, *Grundlagen der. phys.-chem. Petrographie*, 1915, p. 196.) The percentages of MgO, FeO and MnO are calculated to 100 and plotted as shown on Fig. 22. The broken line represents the limits of solid solution.

As before stated some analyses of garnet show titanium: such is often recorded for example in melanite. It is uncertain whether this is really a case of replacement of SiO_2 by TiO_2; whether the titanium may be present as a base in some lower state of oxidation, or whether it is a case of mechanical inclusions; the melanite of the borolanite of Sutherlandshire certainly encloses determinable crystals of sphene, a mineral absent from the rest of the rock. This may be due to reactions occurring in a solid solution below its freezing point, a very common phenomenon in metallic alloys, for example.

The Rhombohedral Carbonates. One of the most striking cases of a complex group of isomorphous minerals is afforded by the very widely spread family of the rhombohedral carbonates, of which calcite may be taken as the type. This occurs in large quantities in a very nearly pure condition, Iceland spar being about the nearest approach known to absolute purity in a natural mineral. In this respect its only rival is the form of quartz known as rock-crystal. There are also found in a reasonable degree of purity the carbonates of magnesia, iron, manganese and zinc, all of which are minerals of economic importance, magnesite as a refractory, the others as ores. There are also known several varieties of rhombohedral carbonates containing two or more of the bases mentioned, as well as, sometimes, smaller quantities of barium, strontium and lead. There is also a cobalt carbonate, which always seems to occur in a concretionary or botryoidal form. Moreover, an interesting problem is afforded by the mineral dolomite, as will appear shortly.

It thus appears that this series contains five fundamental members, the carbonates of calcium, magnesium, iron, manganese and zinc. Of these, zinc usually occurs independently and does not mix with the others to any great extent; moreover, it is nearly always concretionary in habit and not well crystallized, so, as a matter of convenience, the zinc carbonate (calamine) will here be omitted from the general discussion, notwithstanding its importance as an ore. Its occurrence is in many ways rather exceptional.

We are faced, then, with the problem of representing in a satisfactory way an isomorphous series of four principal components and their mixtures or compounds. The obvious method that suggests itself is by means of a tetrahedral model, which of course is the best. But it is necessary to convert such a model into a plane diagram. This can be done by supposing the tetrahedron to lie on one face, and projecting the necessary edges and points on this base, as seen from above: the edges will then be represented by three lines from the corners meeting at the centre of the equilateral triangle. The chief objection, which is not important, is that these edges are foreshortened and therefore not to the same scale as the other three, but the ratio is simple, namely $1 : \frac{\sqrt{3}}{3}$.

Since calcium carbonate is in many ways the most important of the four it is selected for the central position (the top of the tetrahedron) *G*. Then binary compounds or mixtures are represented by points on the edges, such as *D.E* and *F* ternary mixtures by points on the faces, while quaternary mixtures (points within the solid) need hardly be considered.

The following table gives the minerals most usually recognized in this group, with the angles between their cleavages: it will be seen that the greatest variation in these angles in the whole group is only 2½ degrees:

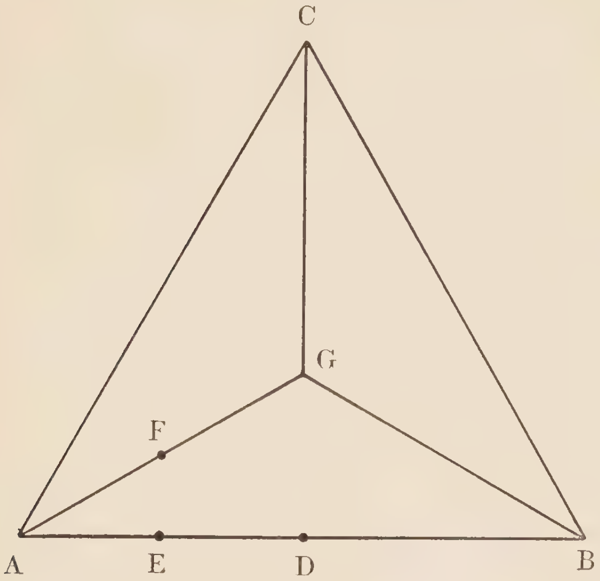

FIG. 37.—The rhombohedral carbonate group: see explanation in text.

Name.	Composition.	Cleavage Angle.
Calcite	$CaCO_3$	74° 55′
Magnesite	$MgCO_3$	72° 36′
Siderite	$FeCO_3$	73° 0′
Rhodochrosite . . .	$MnCO_3$	73° 0′
Dolomite . . .	$CaMg(CO_3)_2$	73° 45′

Other varieties to which names are given are ankerite (Ca, Mg, Fe)CO_3, mesitite $2MgCO_3.FeCO_3$, breunnerite (Mg, Fe)CO_3, pistomesite $MgCO_3.FeCO_3$, manganosiderite (Fe, Mn)CO_3, and manganocalcite (Mn, Ca)CO_3.

It is very doubtful whether mesitite and pistomesite are definite molecular compounds (double salts): they are probably only forms of breunnerite which happened to fall near a simple ratio: manganosiderite and manganocalcite are certainly mixtures. The most interesting and puzzling case is that of dolomite, which must be considered somewhat fully, as it well illustrates a general principle.

It is one of the fundamental principles of true isomorphous series (solid solutions) that the physical characters of the mixtures are linear functions of the concentration. Therefore, knowing the values of some physical constant for the end members it is possible to test, by calculation or graphically, whether a given mixture is a member of an isomorphous series or not ; the formation of a molecular compound (double salt, etc.) is supposed to be always attended by some discontinuous variation of characters. Almost any physical constant can be used for this purpose, those most commonly employed being density or its reciprocal, specific volume ; refractive indices ; birefringence ; or electrical conductivity. Chemical analyses of innumerable specimens of well-crystallized dolomite have shown that in general the composition can be represented as $CaCO_3.MgCO_3$ or $CaMg(CO_3)_2$, which of course indicates the existence of a definite double salt. To test this many careful determinations have been made of the physical properties. The older results all seemed to show that the point indicating the specific volume of dolomite did not lie on the straight line joining those of calcite and magnesite on a *cv* diagram (Fig. 38). However, Spangenberg [1] has investigated the question afresh with the purest synthetic products. For artificial dolomite he found the density to be 2·825, for artificial magnesite 2·958, while the density

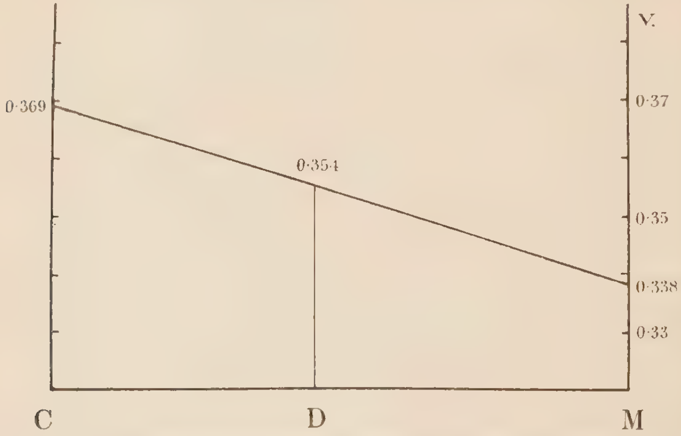

FIG. 38.—The ordinates represent the specific volumes of calcite (*C*), magnesite (*M*), and dolomite (*D*), as explained in text. Abscissæ are percentages of $CaCO_3$ and $MgCO_3$.

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[1] Spangenberg, *Zeits. für Krist.*, vol. lii, 1913, p. 529.

of the purest calcite is known to be 2·714. If the reciprocals of these values are plotted as ordinates against the composition, it is found that the point for dolomite lies exactly on the straight line joining the other two, as required for an isomorphous mixture, and the same is true when the refractive indices are plotted against the composition, the agreement here being remarkably close. But against this we have to set the unquestioned fact that dolomite crystallizes in a class of the rhombohedral system having a lower degree of symmetry than calcite; however, its cleavage angle falls well within the limits for the group, and nearly half way between those of calcite and magnesite. There for the present the question rests, still undecided.

Most of the so-called dolomite-rocks or magnesian limestones are not composed of the pure mineral dolomite alone, but analysis nearly always shows an excess of calcium carbonate over the 1 : 1 ratio. The presence of calcite in them can often also be demonstrated by staining tests.[1] The presence of dolomite in limestones is a matter of considerable practical importance since magnesian lime is unsuitable for many, especially agricultural, purposes. The uses of dolomite as a flux and refractory are discussed elsewhere (see Chap. XI).

Ankerite is a well-crystallized mineral of very common occurrence in rocks of all sorts: it is undoubtedly a mixed crystal, but often corresponds more or less closely to $2CaCO_3.MgCO_3.FeCO_3$. However, no significance can be attached to this formula. Breunnerite certainly belongs to the same category.

The presence of small amounts of the carbonates of barium, strontium and lead in some rhombohedral carbonates is of interest, for a reason that will appear later. These compounds normally crystallize in a more or less pure form in another isomorphous carbonate series belonging to the orthorhombic system.

The Isomorphous Series, Calcium—Strontium—Barium—Lead. These four metals illustrate well the property of general isomorphism in the chemical sense in many of their compounds, and it happens that two series, the carbonates and the sulphates are nearly all minerals of geological and economic importance. Thus we have:

Carbonates.	Sulphates.
$CaCO_3$, aragonite	$CaSO_4$, anhydrite
$SrCO_3$, strontianite	$SrSO_4$, celestine
$BaCO_3$, witherite	$BaSO_4$, barytes
$PbCO_3$, cerussite	$PbSO_4$. anglesite

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[1] Holmes, *Petrographic Methods and Calculations*, London, 1921, p. 264.

The hydrated calcium sulphate, gypsum, belongs to a different crystallographic system and is rather unusual in its relations (see p. 180). Anhydrite also does not agree very closely with the other sulphates.

In both of these series the tendency to the formation of mixed crystals is not very strongly marked, but still it does exist; calcium and barium minerals seem to be fairly miscible, while the other pairs have a more limited miscibility, least so in the case of the lead minerals. It is to be noted here that calcium carbonate occurs in two distinct crystal series: this point is referred to again in the chapter on polymorphism, to which reference should be made for details (see p. 86).

Beside the definite species of carbonate listed above, there is also the mineral bromlite, which appears to be a mixed crystal—$(Ba, Ca)CO_3$: it is only found near Alston Moor, Cumberland. The most unhappily named mineral barytocalcite is commonly believed to be a double salt $BaCO_3.CaCO_3$, but it is monoclinic and is altogether aberrant.

Barytes, celestine and anglesite form an excellent example of an isomorphous series from the chemical and crystallographic standpoint and undoubtedly possess a considerable degree of mutual solid solubility, and calcium sulphate is often also present in apparently homogeneous mixture.

The Wolframite Series. An excellent example of an isomorphous series in minerals of industrial importance is afforded by the wolfram group, the chief ore of tungsten. These minerals are mixtures of the tungstates of iron and manganese, $FeWO_4$ and $MnWO_4$: these compounds when pure are called ferberite and hübnerite respectively. They crystallize in the monoclinic system. Mineralogists of the old-fashioned systematic type have made many endeavours to show that different varieties of the mixed tungstates contain iron and manganese in definite molecular ratios, but it is now clear that they form a continuous series of solid solutions. In accordance with this principle the following system of nomenclature has been proposed.[1] Varieties with from 100 to 80 per cent. $FeWO_4$ are to be called ferberite; with from 100 to 80 per cent. $MnWO_4$ hübnerite, all intermediate types being wolframite. The point is, however, not of much practical importance, since the atomic weights of iron and manganese are nearly equal and the actual percentage of WO_3 in the whole series varies only very slightly—hence the commercial value of all varieties is the same.

Calcium tungstate (scheelite) $CaWO_4$, and some other less common tungstates, e.g. $PbWO_4$ and $MgWO_4$, belong to another isomorphous series, crystallizing in the tetragonal system, and in some of them the tungsten is more or less replaced by molybdenum, forming gradations towards wulfenite, $PbMoO_4$, and other less common ores of molybdenum. Molybdenum however does not seem to enter into the monoclinic wolfram series.

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[1] Hess and Schaller, *Bull.* 583, U.S. Geol. Survey, 1914.

Isomorphism among Ore-minerals. Of especial importance from the practical point of view is the widespread occurrence of mixed crystals among the ores of the metals. In many instances this has a great effect on the value of the ores, since it may introduce a degree of complexity that leads to difficulties in the metallurgical treatment of the ores.

Isomorphous mixture of vicarious constituents is found to a greater or less extent in a very large proportion of the members of the group of ores collectively described as the sulphides; here are included in reality two fairly distinct categories, the primary simple sulphides, such as pyrite, galena or blende, and the secondary, usually more complex double sulphides, such for example as fahlerz and ruby-silver ore. Some simple sulphides like chalcocite, belong to both groups. Closely allied in many ways to the sulphides are the selenides and tellurides, the elements S, Se and Te showing many chemical analogies, and forming a natural series in the periodic table.

It is well known to everybody that a large proportion of the silver production of the world is obtained from lead. Silver is almost universally present in galena, though often only to the extent of a few ounces to the ton, and the question arises, in what form it exists. The sulphide of silver, argentite, Ag_2S, is a cubic mineral in some ways resembling galena, with which it appears to be miscible only to a small extent. Recent American studies by metallographic methods have shown that in argentiferous galena of low grade the silver is invisible and therefore in solid solution, whereas in some specially rich samples the argentite can be seen as thin flakes and strings along the cleavage planes of the galena. Thus it is shown that at the ordinary temperature the solubility of argentite in galena amounts only to a small fraction of 1 per cent. There is thus some analogy to the behaviour of metallic silver and lead, as shown in the Pattinson process.

Some very striking examples of double isomorphism are shown by the complex sulphantimonides and sulpharsenides of copper and silver, some of which are important ores. It is impossible here to mention all of these, and two groups only will be chosen as typical examples, namely fahlerz and ruby silver. These mineral series are also of much interest as examples of intermolecular compounds of two end products in definite stoichiometric proportions.

The Fahlerz Group. The general formula of this group may be written as $4R'_2S.R'''_2S_3$. In this formula R' may be Cu, Ag, Hg, Zn, Pb, Mn, and more rarely Co and Ni. The acid-forming radical R'''_2S_3 may contain either Sb, As, or Bi. The most typical members of the group are nominally tetrahedrite, $4Cu_2S.Sb_2S_3$, and tennantite, $4Cu_2S.As_2S_3$, which form a continuous mixed-crystal series. An argentiferous variety, sometimes called freibergite, may contain up to 30 per cent. of silver, and a large proportion of the legendary wealth of the Spanish-American colonies of the early days came from this source. A rare variety called schwatzite from the Tyrol and elsewhere has been worked as an ore of mercury, which may run up to 17 per cent. Occasionally some of the sulphur in any variety may be replaced by selenium.

Ruby Silver Ores. This group includes the two well-defined minerals pyrargyrite, $3Ag_2S.Sb_2S_3$ and proustite, $3Ag_2S.As_2S_3$. They crystallize in the rhombohedral subdivision of the hexagonal system, like calcite, but commonly show different habits. It seems however that mixed crystals are formed only to a small extent, the isomorphism being very limited.

The Telluride Ores. In three important gold-producing regions of the world, namely, Western Australia, Hungary and Transylvania, and Cripple Creek, Colorado, the chief ore consists of various compounds of gold and tellurium, nearly always with a good deal of silver in solid solution. The telluride minerals form a complicated series, but can for the most part be reduced to two fundamental types, namely R_2Te, and RTe_2, in which R may be gold or silver in any proportion, rarely mercury. A large number of somewhat unnecessary names have been applied to different varieties, such as calaverite, sylvanite, krennerite, petzite, nagyagite and so forth.

The Relations of Gold to the Sulphides. A large amount of gold is obtained from ore-minerals of the sulphide group, using the term in its broadest sense to include related mineral families, such as the arsenides. Gold is not known, however, to form sulphides, arsenides or selenides as separate compounds, and there is much doubt as to the condition in which it exists in these minerals. It is certainly present in some form of solid solution, but the chief point at issue is as to whether the gold exists as the metal, or whether it actually forms sulphides, selenides or arsenides which are dissolved to a small extent in the corresponding base metal minerals. Nearly all pyrite carries more or less gold in some form, and the slimes obtained in the electrolytic deposition of copper from chalcopyrite and cupriferous pyrite are an important source of the metal. The chief gold ore of some of the great mines of Brazil for example (St. John del Rey and Passagem) is auriferous arsenopyrite (FeAsS) and in Sumatra gold is worked in association with selenium. This shows an approximation to the telluride type.

Even the native gold of the quartz veins and other deposits of the same general type is always more or less alloyed with silver, and the existence of amalgams, compounds of gold or silver and mercury, is well known. Thus gold shows a strong tendency to solid solution in various forms, a matter of much importance in ore-dressing and metallurgy.

CHAPTER IV

POLYMORPHISM

Dimorphism in Minerals. It has long been known to mineralogists that a large number of definite chemical compounds or even elements occur in nature in two or more forms, which although possessing identical compositions so far as analysis can show, yet have different physical properties. In some instances we are acquainted with both amorphous and crystalline varieties, as in the three forms of carbon, charcoal, graphite and diamond. In other instances all the forms are crystalline, as with rutile, anatase and brookite, or andalusite, kyanite and sillimanite. It is now known that silica can exist under different conditions in at least seven distinct crystalline modifications, as well as in an amorphous glassy form. The whole trend of recent research has been to show that similar relations are extremely common in minerals, and many of the instances now discovered are of considerable practical importance.

One of the most noticeable features in connection with this subject is the fact that very commonly in nature two or even more forms of the same substance are found existing side by side, apparently in a state of complete stability. It is quite clear, however, that in such cases one or the other form must be in an unstable condition of equilibrium although the transformation may be completely in abeyance. This phenomenon of lag in adjustment of equilibrium is a very common occurrence in the mineral kingdom, as is reiterated almost to the point of weariness in many sections of this book: here it is specially conspicuous.

Some very curious effects are to be noted in certain mineral structures formed as parts of the external or internal skeleton of animals. Thus when calcite and aragonite are both being secreted from the mantle of one small mollusc it is obvious that they cannot both be in equilibrium with the same environment; still both are formed. Again the complete belemnite as usually found consists of a phragmocone of aragonite and a guard of calcite, both forming parts of one internal structure. As a matter of fact the relations of calcite and aragonite are still very obscure.

The subject under discussion in this chapter is mainly the existence in nature of these varying forms of the same compound; the laws governing their fields of stable and unstable existence; and especially the conditions of the transformations from one form to another. Certain examples of high scientific interest or technical importance are dealt with in more detail elsewhere: here most attention will be paid to general principles.

When a substance exists in two forms it is said to be dimorphous, in three forms trimorphous, and so on: the general name of the phenomenon is *Polymorphism.* The conditions governing the range of stability of the different forms are temperature and pressure, and the transformations involved show a close analogy to the changes between the liquid and solid states, being amenable to treatment on the same principles of thermodynamics. The chief general principle is this: that the different forms of the same substance having different physical properties, must contain different amounts of energy: this is shown by the fact that the transformations are accompanied by thermal effects, just as in freezing and melting. Further at the transition points the different forms are in equilibrium and must then contain an equal amount of energy. Certain other conclusions follow; e.g. the unstable form must contain the larger amount of energy and therefore, as can be shown theoretically and confirmed by experiment, must possess greater solubility. Since the polymorphs nearly always have distinctly different densities, the effect of pressure on their transformations can be predicted from Le Chatelier's principle, since pressure will obviously favour the formation of the denser form. Similarly rise of temperature will cause endothermic reactions and vice versa. Hence it follows that the equations governing changes in the solid state are similar in form to those relating to freezing and melting. In fact the general Clausius–Clapeyron equation

$$\frac{dt}{dp} = \frac{T(v_2 - v_1)}{Q}$$

is here strictly applicable, where v_1 and v_2 are the volumes of the two forms, and Q, which may be either positive or negative, is the thermal effect, T being the absolute temperature.

In the case of simple substances, systems of one component, the chief effect of polymorphic transformations is to produce a break in the curves expressing their physical properties, for example, the freezing point.

Enantiotropy and Morphotropy. Polymorphic transformations of crystalline substances can be divided into two categories according to whether the transformation is reversible or not. In the first class, called enantiotropic, the transition point from one solid form to the other lies below the melting-point: only under these conditions can true equilibrium exist at the transition point between the two solid forms, both of which can be obtained in a stable condition within their appropriate range of temperature and pressure. The relations here prevailing can be conveniently shown by plotting the vapour pressure curves of the two forms and of the liquid on a *pt* diagram (Fig. 39). Here LK is the vapour-pressure curve of the lower form, which may be called the α-form;

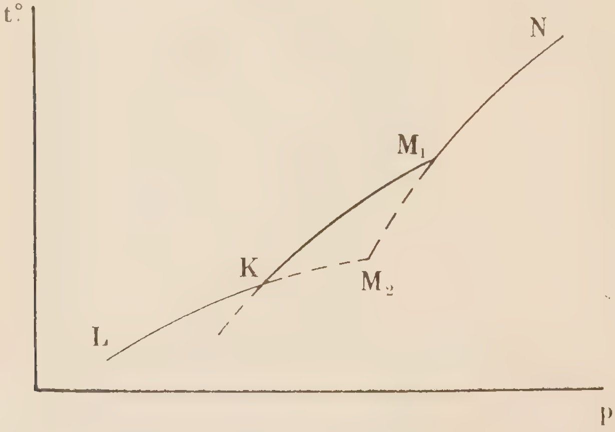

FIG. 39.—Melting-point and vapour-pressure curves of an enantiotropic substance.

The transition point K lies below the melting point M_1 of the high-temperature form. M_2 represents the (unrealizable) melting point of the low temperature form.

K is the transition point, KM_1 the curve for the β-form, and M_1 the melting-point, which is obviously that of the β-form. M_1N is the vapour-pressure curve of the liquid. By prolonging the curves LK and NM_1 till they meet in M_2, a point is obtained, which if realizable would be the melting point of the α-form. Although KM_2 and M_1M_2 represent unstable conditions, sometimes, owing to delayed equilibrium they can be partly realized. The point is here that LK and KM_1 represent fully stable equilibria, and therefore can be followed in either direction through the inversion point.

In Fig. 40, which represents the conditions for monotropy, corresponding points are similarly lettered. The true transformation point, if it could be attained, is above the melting point of either form. It is also clear from the figure that one of the solid forms shows no point of stable existence, and since it is not possible for a stable form to alter into an unstable form, the transformation is irreversible, and can only take place from curve HM_2 to curve LM_1, for example. Between M_2 and K the unstable form would change to liquid M_2N. Hence it follows that in a monotropic system there can be no true equilibrium between the two solid forms, as there is at the inversion point in an enantiotropic system.

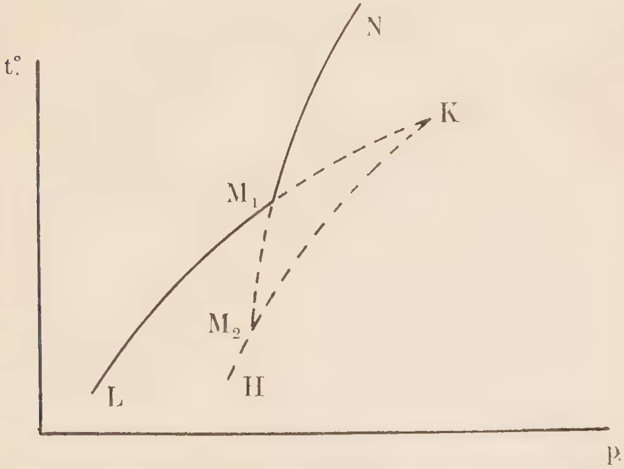

FIG. 40.—Melting-point curves for a monotropic substance.
Corresponding points lettered as in Fig. 39. The transition point is above the melting point.

Inversions. Reference has already been made in Chapter I to the existence of several different forms of ice, at least one of which, besides the common form, is of possible geological interest. Fig. 41 shows in a slightly diagrammatic form the relation of the stability fields of the five known forms of ice in a *pt* diagram. It will be observed that the field of Ice III, the most important of the high-pressure forms geologically, shows the special peculiarity of being limited on all sides.

With reference to the effect of a dimorphic inversion on the course of crystallization of a simple binary eutectiferous system the following points are to be noted. A distinction must be drawn between the cases where the inversion temperature lies above or below the eutectic point.

The case where it lies above the eutectic point will be considered first. An inversion involves a change in the physical properties of the solid form of one component, including of necessity an alteration of the latent heat of fusion. Since the latent heat of the solvent is one of the variables in the equation governing the lowering of the freezing point, it follows that a sudden change in this quantity must show itself in an inflection of the freezing-point curve (Fig. 42), while the nature of the solid in equilibrium with liquid in the area $gEDT_bT_i$ will be different above and below the line DTi. Some such point as $T_{b'}$ will represent the (unstable) freezing point of the α-form of B. Further, it is conceivable that the curve T_bD might be continued downwards in unstable equilibrium, so as to cut the unstable prolongation of T_aE and thus to produce a false eutectic of the β-form of B and A, having a position quite different from that of the real eutectic of α-B and A.

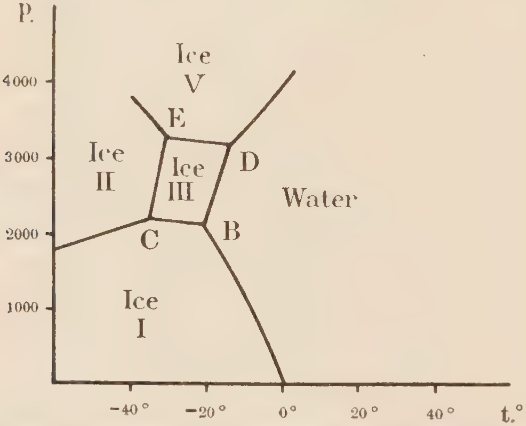

FIG. 41.—Fields of stability of the different forms of ice at pressures up to 4,000 atmospheres, mainly from data given by Tammann.

B is the triple point for ordinary ice, Ice III and water: the field of existence for Ice III is given by the quadrilateral $EDBC$. (After Boeke.)

In the second case where the transition point lies below the eutectic point, the relations are much simpler, since the α-form of B can never be in contact with liquid. All that is necessary to show the stability fields is to draw an isotherm through the transition temperature; as in Fig. 43. This case occurs in the alumina-silica system, where the inversion point sillimanite-andalusite comes below the eutectic temperature, though its exact position is not known.

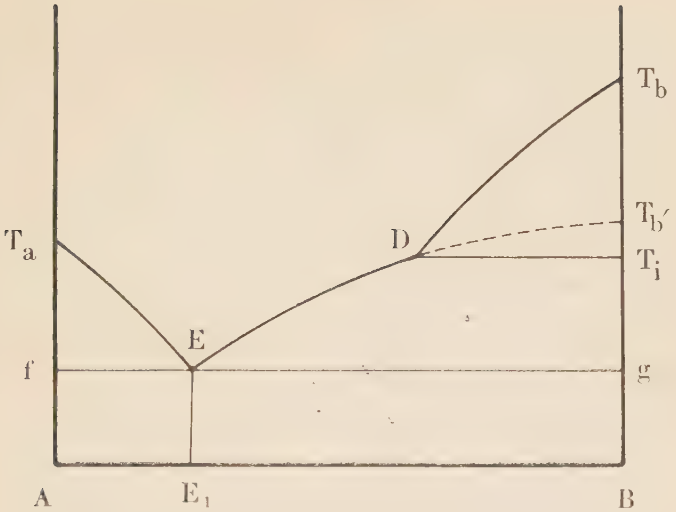

FIG. 42.—Equilibrium diagram for a binary system where one of the components undergoes an inversion at the temperature T_i above the eutectic temperature.

Incongruent Melting. Somewhat allied to the foregoing is the phenomenon known as incongruent melting, where a binary compound has no real melting point, but on heating splits up into another solid of different composition and a liquid. This occurs

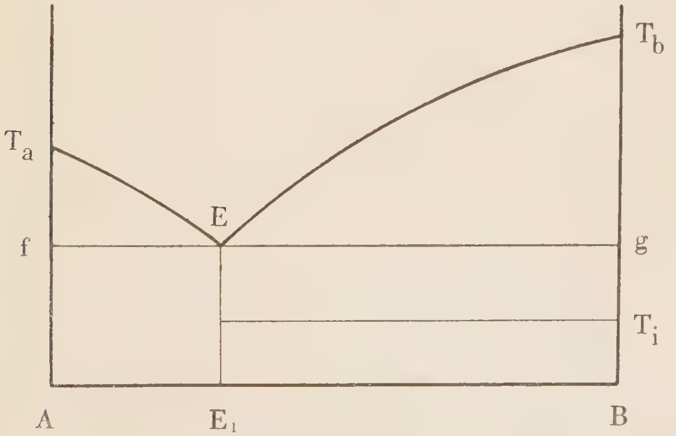

FIG. 43.—Equilibrium diagram for a binary system where one of the components undergoes an inversion at a temperature T_i, below the eutectic temperature.

sometimes when two substances A and B combine in more than one ratio to form intermolecular compounds, say A_mB_n, and A_pB_q. One of these will show as usual a maximum on the melting-point curve, but corresponding to the other there is only what is called a " hidden maximum " which cannot be realized in stable equilibrium : since before this temperature is reached the mineral splits up into a mixture of the other compound and liquid. These relations are shown in Fig. 44, where K is the transition point and x the " hidden maximum." Here A_pB_q is stable only up to the temperature of the isothermal through K and splits up into A_mB_n and liquid. This effect is well known in clinoenstatite, which is partly converted to olivine on heating, and a similar phenomenon has recently been described by Bowen in the melting of orthoclase, which yields leucite. The practical effect is that it is impossible to obtain a pure melt direct from such minerals : they must pass through an intermediate solid stage of different composition. All this is of greater importance in cooling, in that the first-formed high temperature mineral may later react with the liquid and become coated with a skin of the other compound. In theory the conversion should be complete, but very often not sufficient time is allowed for establishment of true equilibrium and a zonary structure results. The first-formed zone naturally serves to protect the core from further reaction. This accounts for the very common fringes of enstatite round olivine crystals (kelyphitic or corona structure : see also p. 122).

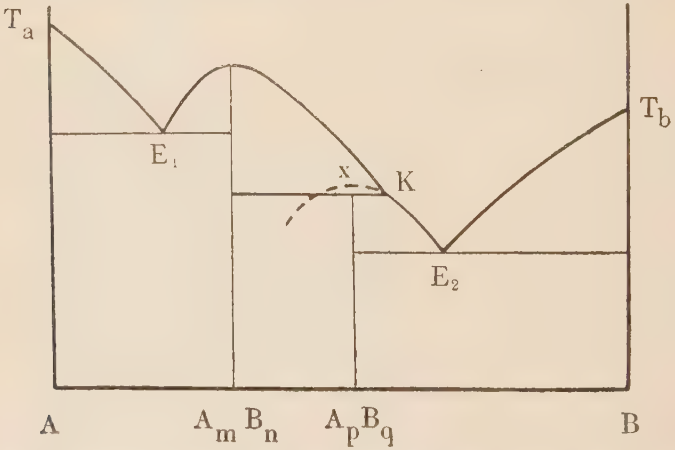

FIG. 44.—A binary system, with two molecular compounds, one of which shows incongruent melting at K.

There is obviously a very close analogy between the phenomena here described and the behaviour of salt hydrates in solution. It has already been shown that in some cases the solubility curve of salts undergoes not only an inflection, i.e. change of slope, at a transition point, but even a change of direction (change of sign), as in calcium sulphate and sodium sulphate. In a similar way it is possible theoretically for the freezing-point curve of a liquid to undergo a change of direction at an inversion point. This condition is realized in the case of water, Ice I and Ice III at the triple point. Ice I is lighter than water and therefore its freezing point is lowered by pressure, but Ice III is heavier than water and its freezing point is therefore raised by pressure. Hence the curve undergoes a complete change of direction, as shown at B in Fig. 41, the co-ordinates of the point being $-22°$ and 2,050 atmospheres.

With regard to the relations between the different polymorphic forms of the same substance, very little of a general character can be said in the present state of our knowledge. There is one point, however, arising from empirical observation, that may profitably be noted, namely that in at any rate the majority of known instances, the higher-temperature form possesses the higher degree of crystal-symmetry. This point is very well illustrated in the silica system. (For details, see p. 216.) There is as yet scarcely sufficient material in hand to justify a generalization with regard to the effect of pressure on symmetry. There is every reason to believe that kyanite is the highest-pressure form of aluminium silicate and it has the lowest symmetry of the three forms. Since quartz has the smallest specific volume of the forms of silica it is naturally stable at high pressures, as in metamorphic rocks; it is rhombohedral, while tridymite is hexagonal and cristobalite cubic (at high temperatures).

Fluxes in Mineral Synthesis. It is well known that some minerals, abundant in nature, cannot be obtained artificially from a so-called " dry melt," that is to say, by simple fusion and crystallization of a mixture of their constituents in proper portion. It is often found that this process gives rise to a crystalline product having the proper chemical composition, but forming a mineral species not known to occur naturally. This is the case for example with such common substances as the calcium and magnesium metasilicates, which form pseudowollastonite and clinoenstatite respectively, instead of the natural minerals wollastonite and enstatite. Another very prominent example occurs among the various polymorphic forms of silica, as discussed in detail in Chapter XI. In dry melts the form most commonly obtained is tridymite, sometimes cristobalite, but never quartz. However, it is found that when certain substances, acting as fluxes, are added to the melt the normal mineral can be obtained : sometimes water alone is sufficient, but this involves special arrangements for heating under high pressures, such as the employment of heavy bombs and steel cylinders, both difficult and dangerous work. Much easier and quite as effective is the employment of some such substances as sodium tungstate, calcium vanadate or even sodium chloride, which can be used at ordinary pressures.

The whole principle involved can be summed up in a few words : there is a definite temperature at which the two forms of the mineral in question undergo inversion ; this inversion temperature is below the freezing point of the higher-melting artificial form from a pure melt. The effect of the flux is to lower the freezing point below the inversion temperature into the region of stability of the other form. These relations can be shown very simply as in Fig. 45, where the abscissæ represent percentages of the flux added to the melt and ordinates are temperatures. By Van't Hoff's law the lowering of the freezing point is proportional to the amount of flux added, but it is found that the addition of a flux does not alter the inversion-temperature : hence the freezing-point curve must somewhere cut the inversion-isothermal. With a proportion of flux higher than is represented by the *c* co-ordinate of this point of intersection the second mineral form must crystallize out. This principle may obviously be extended to any number of transformations of polymorphic minerals. In the case of silica the relations are very complex, since each of the minerals quartz,

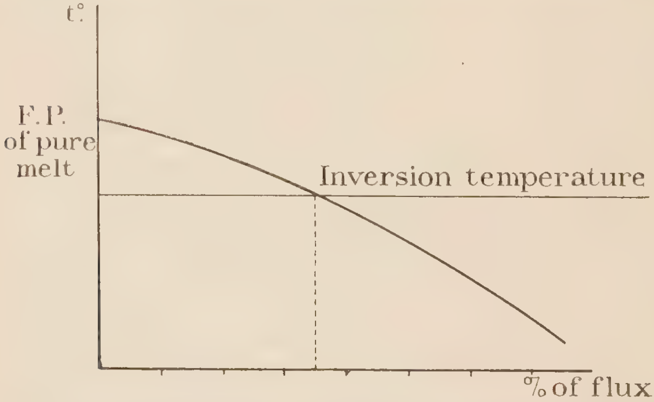

FIG. 45.—This shows the successive depression of the freezing point of a pure substance below the inversion temperature by addition of increasing quantities of a flux.

tridymite and cristobalite possesses at least two forms, and some of the inversions occur at very low temperatures, between 100° and 200°.

Dimorphous and Polymorphous Minerals. Having now dealt with the general physico-chemical principles concerned in the study of polymorphism, it only remains to mention a few examples. Several instances of a striking character are discussed somewhat fully in the various sections of this book, especially the silica system, the pyroxenes and the aluminium silicates, so that no more need be said about them at this point. There remain, however, many other instances of common occurrence and great interest, as to which a few words may well be said here.

Titanium Dioxide. This substance commonly exists in three different forms, rutile, anatase, and brookite: unfortunately very little is known as to their mutual relations and fields of stability. Numerous synthetic researches, some carried out by Daubrée as long ago as 1849, all of which appear to have involved the use of some flux, show in general that rutile is formed at the highest temperatures, brookite at temperatures considerably lower, while these experiments, and numerous observations in sedimentary rocks show clearly that anatase can be formed at or very near atmospheric temperatures and pressures. For example, small and perfectly formed crystals of anatase, obviously formed in place, are abundant in the ironstones of Cleveland [1] and Frodingham, Lincs.[2] which have certainly never been metamorphosed in the least degree. It is quite clear that the titanium dioxide minerals are all very closely related, and that transformations may occur in almost any direction. Rutile has often been observed as a primary constituent of igneous rocks, and seems to be in general the most stable phase, as witness its very great abundance in clastic sediments. Here it must of necessity be really in unstable equilibrium, but the velocity of inversion seems to be infinitely small. There is reason to believe that anatase and brookite are in reality mainly formed from ilmenite and not by inversion of rutile.

The Iron Disulphides: Pyrite and Marcasite. Here we are on somewhat firmer ground, since there are a certain number of experimental facts, as well as empirical observations of these two very common minerals. Nevertheless the evidence available leads to some very conflicting and curious results. In the first place the iron disulphide of the igneous rocks is always pyrite, which in many places occurs in enormous masses as a differentiation product of basic magmas, or in some cases perhaps as a replacement due to hydrothermal magmatic solutions. (Huelva district, Spain ; Rorös and Sulitjelma, Norway ; Chessy, France ; Bielorechinsky, Urals, and many others.) Pyrite is also perhaps the commonest sulphide in mineral veins and is abundant in many metamorphic rocks. It is therefore formed at moderate and high temperatures. On the other hand marcasite is very abundant in entirely unmetamorphosed sediments, e.g. the Gault at Folkestone and the Chalk everywhere. But here we come up against the curious fact that though marcasite is clearly formed at the normal temperature and pressure it is exceedingly unstable under such conditions, easily oxidizing to ferric hydrate and sulphuric acid in damp air. This decomposition quickly takes place spontaneously in museum cases. Pyrite also undergoes a similar decomposition but much less readily ; it is quite stable in collections, and apparently often so in the open air. Owing to certain peculiarities in the electrical behaviour of pyrite, there is at any rate room for suspicion that two different polymorphic forms are here included under one name : this idea is strengthened by curious variations in the stability of different specimens subjected to similar conditions, either naturally or artificially. At any rate it is clear that pyrite is the stable form at high temperatures and its symmetry (cubic) is higher than that of marcasite (orthorhombic).

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[1] Dick, *Iron Ores of Great Britain*, Pt. I., Mem. Geol. Survey 1856, p. 97. Stead, *Cleveland Inst. Engin.*, 1910, p. 89 and Fig. 13.

[2] Author's observations.

Calcium Carbonate. This substance occurs in two distinct crystalline forms, calcite and aragonite. Many attempts have been made to prove the existence of other crystalline polymorphic forms, but hitherto none of these can be regarded as satisfactorily established. They will not be considered further here. The relations of calcite and aragonite are peculiar and have never been explained. In purely mineral occurrences as apart from organic structures, calcite is by far the commoner, and in most situations it is undoubtedly the stable form. It occurs in immense quantities in many vein-deposits, metalliferous and otherwise, and in all limestones that have become to any extent crystalline, including not only all true marbles, but many calcareous rocks that have only undergone a very slight degree of alteration. It is also the only form in various groups of organisms, especially the echinoderms, many of which, e.g. crinoids, are of great importance as rock-builders. It has also lately been shown that calcite occurs as an apparently primary mineral in certain peculiar igneous rocks.[1] On the other hand aragonite is found in some quantity in certain mineral veins, to a large extent in the deposits of hot springs (Karlsbad, Vichy, etc.), while it constitutes the whole solid skeleton of corals, therefore forming a large part of modern coral reefs: it is also common forming the whole or part of some molluscan shells, especially the pearly layer. Calcium carbonate is also abundant in many limestones, as for instance the Chalk, in what appears to be an amorphous form, though this lack of apparent crystalline structure may in reality be due to an extremely fine state of division.

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[1] Brögger, *Die Eruptivgesteine des Kristianiagebietes,* Part IV. *Das Fengebiet.* Kristiania, 1920.

One thing at any rate is clear, that on the slightest disturbance of equilibrium there is always a marked tendency for aragonite to recrystallize as calcite. All the calcium carbonate of the metamorphosed rocks is calcite, even in those crystallized under pressure, and this is where the chief physico-chemical difficulty comes in, since aragonite is denser than calcite and should therefore be stable under high pressures. However, observation shows that it is not. The explanation of this anomalous behaviour is as yet to seek.

With regard to conditions of formation, it is known that calcium carbonate deposited from hot solutions is aragonite, from cold solutions calcite, and this suggests that all aragonite at the normal temperature is metastable: this idea, however, in no way explains its behaviour at high pressures: its stability field must be very peculiar in some way not yet understood. It seems possible, however, that certain anomalies in the specific heats of calcite and aragonite, and the very small heat effects on transformation may eventually afford an explanation. Since the volume-difference is very large, $\frac{1}{2{\cdot}94}$ and $\frac{1}{2{\cdot}71}$ respectively, and the heat-effect very small, it follows from the Clausius equation that the effect of pressure on the transition point must be large, and it is possible that aragonite is only truly stable at high pressures. Unfortunately no measurements of the heat of inversion are available, so that the problem cannot be solved quantitatively.

Hornblende and Augite. In a general way the amphiboles and the pyroxenes seem to form a dimorphous series and some varieties even appear to be trimorphous. Another case here appears to arise since igneous rocks, such as dolerite and basalt, rich in augite, are converted by dynamic metamorphism into amphibolites or hornblende-schists. Here again we are confronted by the fact that hornblende, the form stable under pressure, has a larger specific volume than augite. But in this instance it is by no means clear that the original augite and the secondary hornblende have the same chemical composition. In all probability there is considerable addition or subtraction of constituents, probably both, since as a rule the composition of amphiboles seems to be more complicated than that of the pyroxenes, and the occasional presence in both of alumina, and of the elements of water, perhaps as OH, in some hornblendes is not really understood. Hence not much stress can be laid on this apparent contradiction of thermodynamic principles.

Carbon. The classical example of trimorphism is afforded by the three forms of carbon, charcoal, graphite and diamond. The whole subject of their relations is highly speculative and cannot be discussed with much profit. At any rate it seems clear that diamond is a high-pressure mineral, and it can undoubtedly only be formed at high temperatures. We are therefore driven to conclude that under normal conditions diamond is unstable. This unstable state is, however, extraordinarily persistent: indeed, the resistant properties of the diamond are proverbial. It is characterized by an extraordinary degree of hardness, high density, very high refractive index and dispersion; in fact all its properties are exaggerated. Graphite crystallizes at high temperatures; e.g. in metamorphic rocks and in iron and steel, while amorphous carbon occurs in nature in coals and other sedimentary rocks, one of the purest forms being anthracite. With regard to graphite and diamond the law of increased symmetry holds (hexagonal and cubic). It was formerly believed that diamond crystallized in the tetrahedral class of the cubic system, but recent X-ray work has shown that it in reality possesses holohedral symmetry.

Polymorphism in General. It is unnecessary in this book to give a discussion of other cases of polymorphism, such as the well-known instances of phosphorus and sulphur. Of the numerous forms of the last-named that are now known only one occurs in nature, the ordinary rhombic sulphur, as seen in crystals found in volcanic regions, e.g. Sicily. Numerous investigations have shown that polymorphism is an exceedingly common phenomenon in substances of all classes, both natural and artificial. It is necessary, however, to draw a distinction between true polymorphism, the existence of two or more definite crystalline forms of one substance, and the possible existence of both crystalline and amorphous forms of the same substance. In true polymorphism the change from one form to the other under definite physical conditions is undoubtedly connected with the equilibrium of different forms of space-lattice; particular arrangements of the molecules or atom-groups becoming unstable when conditions pass certain limits and passing over into other forms better adapted dynamically to withstand the strains set up. In this change energy is set free as work and shows itself as a heat-effect. But in amorphous substances there is no regularity of arrangement, so far as is known : there is always, however, the possibility that the so-called amorphous state of crystallizable substances has no real existence, but always consists of ultra-microscopic crystalline particles, such particles in true solids, as opposed to undercooled liquids of high viscosity (glasses), being too small to show their character by optical methods.

Isodimorphism. This subject belongs rather to detailed systematic mineralogy than to geology, but should be briefly mentioned here. Several instances are known where series of mixed crystals exist in two different crystalline forms, that is to say, each possible mixture is dimorphous. This phenomenon is perhaps best displayed among the sulphides and arsenides of iron, cobalt and nickel, several of which crystallize both as cubic crystals of the pyrite group and as orthorhombic crystals of the marcasite group. There are also traces of it in the rhombohedral and orthorhombic carbonates, though only to a very limited extent.

CHAPTER V

THE IGNEOUS ROCKS

Composition of the Igneous Rocks. It is a fact scarcely in need of extended demonstration that a large proportion of the rocks constituting the visible crust of the earth have solidified from a molten condition. The process can be seen in actual operation in many volcanoes. Accounts can often be read in the newspapers of flows of molten lava from Vesuvius and Etna, while the great craters of Kilauea and Halemaumau (Mauna Loa) in Hawaii are among the most wonderful natural phenomena in the world. These are only a very few among many examples. After eruption and on cooling the lavas solidify to rocks exactly like many of those now found among the older formations in nearly all parts of the world. Besides these surface flows there are innumerable examples of rock-masses, obviously injected into the crust, at a greater or less depth from the surface, but so similar to solidified lavas that their common origin is clear.

The first point then is, that igneous rocks were once liquids: the second point is that chemical analysis shows that in all cases the dominant constituent is silica, which rarely falls below 40 per cent. and is commonly much higher, often up to 75 or even 80 per cent. It is clear then that the original material of the igneous rocks is to be regarded as a silicate solution. In all probability all, or nearly all, the known elements do actually occur in the igneous rocks, but many of them in very small quantities, and the number of constituents that form each more than 1 per cent. of the whole in normal cases is quite small, not more than a dozen. This fact simplifies the study of the igneous rocks a good deal, although it still remains quite sufficiently complicated. As a matter of practical convenience it has become the custom to state the chemical composition of rocks as shown by analysis in terms not of elements, but of oxides. All the common rock-forming minerals contain oxygen, and it is only some of the rarer constituents that occur as elements, sulphides, or other non-oxygen compounds.

The following table, by F. W. Clarke,[1] shows the average composition of the igneous rocks of the world ; it is obtained by the summation of an immense number of analyses, and probably approaches very closely to the true value. As here reproduced all the rare constituents, as given in the original, are omitted.

SiO_2	59·14
Al_2O_3	15·34
Fe_2O_3	3·08
FeO	3·80
MgO	3·49
CaO	5·08
Na_2O	3·84
K_2O	3·13
H_2O	1·15
TiO_2	1·05
	99·10

Thus it is seen that ten oxides constitute over 99 per cent. of the total. A similar computation by Washington[2] of earlier date, led to an almost precisely similar result, and it may now be taken as established that the average igneous rock contains about 60 per cent. of silica. As before stated, however, there are considerable variations in individual cases : on these variations in silica percentage the classification and systematic study of the rocks largely depends, since the variations express themselves not only quantitatively but qualitatively, in the mineral composition of the rock ; in other words, the kind of mineral formed from a silicate solution depends not only on the constituents present, but also on the ratio between those constituents, and especially on the ratio of silica to bases. A concrete example will make this point clearer. Silica and magnesia can combine in two proportions, as $MgO.SiO_2$ or as $2MgO.SiO_2$. When silica is in excess the metasilicate $MgSiO_3$ (enstatite) will be formed ; when magnesia is in excess Mg_2SiO_4 (olivine) is formed.

The Chemical Constituents of the Igneous Rocks. An examination of the list of chemical constituents of rocks, as set forth in the foregoing generalized analysis, will show that they can be arranged in natural groups, on the basis of valency and chemical affinities, as follows :

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[1] *The Data of Geochemistry*, 5th edition, *Bull.* 770, U.S. Geol. Survey, 1924, p. 29.

[2] "The Chemistry of the Earth's Crust," *Journ. Franklin Inst.*, vol. 190, 1920, pp. 757–815.

1. Silica, SiO_2 ; titania, TiO_2.
2. Alumina, Al_2O_3 ; ferric oxide, Fe_2O_3.
3. Magnesia, MgO ; ferrous oxide, FeO ; lime, CaO.
4. Potash, K_2O ; soda, Na_2O ; water, H_2O.

(As titanium is of much less importance than the others, it will for the most part be ignored in what follows.)

Among these oxides silica is pre-eminently the acid-former : in many important minerals alumina appears to enter into complex aluminosilicic acid radicals, but it also functions as a base ; the other oxides of lower valencies are distinctly basic in their character. Another important point is that the members of each group are to a great extent isomorphous among themselves. .

From this point of view then the raw material of an igneous rock is to be regarded as a silicate melt, or mutual solution of the above-named chemical constituents in varying proportions. Such a melt is conveniently called a *magma*. From this molten magma the minerals separate with compositions and in an order determined by the ordinary thermodynamic laws of solution as controlled by temperature and pressure. From this point of view the magma is to be regarded as a multiple system of many components, and the whole subject is highly complicated.

In the ordinary way, however, the composition of magmas does not vary indefinitely : in point of fact the actual known range of variation is distinctly limited, and this is a subject which must now be considered briefly.

In the first place it is desirable, if possible, to find some method of graphic representation to express these variations : this can be conveniently done as follows. It is generally agreed that silica is the characteristic constituent of igneous rocks, and its amount is made the basis of the scheme. The foundation of the diagram in Fig. 46 is a system of two equal rectangular co-ordinates (in practice, of course, it is a square) with two adjoining sides each divided into 100 parts. The foundation of the idea is this : the abscissæ represent silica percentages in analyses of individual rocks, while the ordinates represent the sum of all the chemical constituents,[1] including silica, divided up into the proper proportions, corresponding points on different ordinates being joined to form curves. For the sake of simplicity in this particular example the ordinates are divided only into four parts, each representing the *sum* of all the constituents of one group as set forth in the list below.

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[1] In fact, the total composition is plotted against silica.

1. SiO_2.
2. $Al_2O_3 + Fe_2O_3$.
3. $MgO + FeO + CaO$.
4. $K_2O + Na_2O + H_2O$.

In such a diagram every possible silica percentage from 0 to 100 is obviously represented by some point on the diagonal line from corner to corner of the square and the height of the silica ordinate must necessarily be equal to the distance of its base from the zero point. It has before been mentioned that the silica percentages of common rocks range only between about 40 and 80 per cent.: hence only a part of the diagram is actually occupied by ordinates. The sum of these ordinates as represented by the curves obviously represents the variation in each particular group of constituents in correlation with variation in silica percentage, a very useful basis of classification. At a later stage this method will also be found very serviceable in the comparison of different rock-groups. Its particular merit at this stage is that it serves to bring out clearly the very limited range of variation existing in

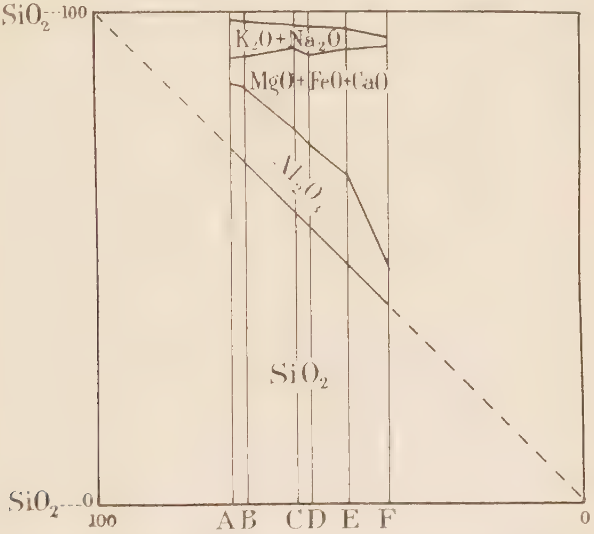

Fig. 46.—The average chemical composition of the known igneous rocks; explanation in text.

A, alkali-granites; *B*, normal granites; *C*, tonalites; *D*, diorites; E, gabbros; *F*, peridotites. (Data from Daly, *Igneous Rocks and their Origin.*)

normal igneous rocks. The points in this actual example are taken from several "composite analyses" or average analyses of a few of the most common rock-types.

It is often useful also to plot the variations possible within a group of rocks, large or small, by another and slightly different method. Here, as before, the silica percentages are taken as abscissæ, and each of the other constituents as ordinates, thus giving a series of independent curves, and showing the individual variations of each constituent more clearly than by the first method. Fig. 47 shows the same data as given in Fig. 46.

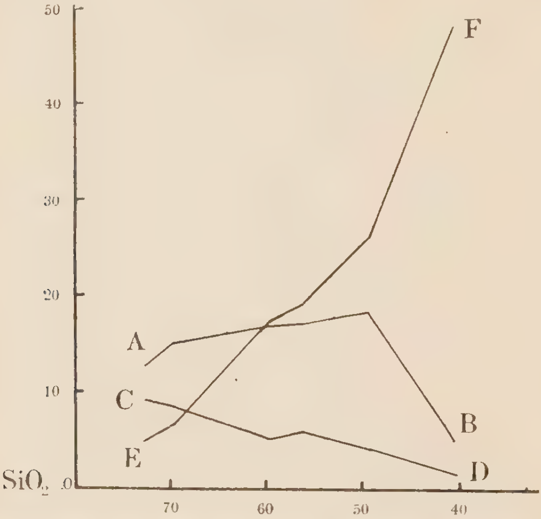

FIG. 47.—This shows the same facts as in Fig. 46, plotted by a different method, as explained in the text.

The two dominant Rock Groups. From diagrams of the kind just considered some very useful conclusions can be drawn. Some most valuable results have been obtained by plotting the sum of the potash and soda against silica, as obtained from a very large number of individual analyses of different rock types. In such a diagram any single rock is obviously represented by a point, and these points can afterwards be generalized into a curve, showing variation of alkalies as correlated with variation of silica. Now when such a diagram is made from a large number of analyses of rocks from all parts of the world, it is found that the points arrange themselves in such a manner that they can only be generalized satisfactorily by means of *two* curves. The general idealised form of these curves is shown in Fig. 48. It will be seen that in one case the percentage of total alkalies ($K_2O + Na_2O$) falls pretty steadily from the acid to the basic end of the series, whereas the other curve rises to a well-marked maximum about the middle and then falls rapidly to the basic end. These two curves correspond to a very real difference in the chemical and mineralogical characters of the rocks. Those represented by the higher curve constitute what is conveniently and obviously known as the *alkaline* series. The other group, being comparatively poor in alkalies, are correspondingly rich in lime, and are therefore known as the *calc-alkaline*, or sometimes as the subalkaline or as the calcic series : the former term is generally preferred. From the run of the curves in Fig. 48, it is of course clear that the differences are most strongly marked in the rocks of intermediate silica percentage, diminishing towards the extreme types. In these intermediate rocks mineralogical differences are very marked.

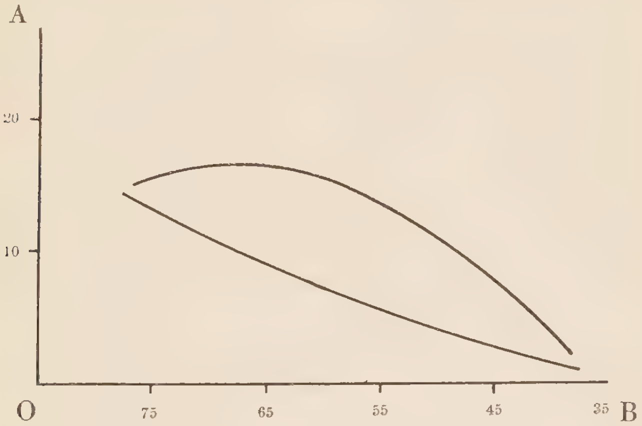

FIG. 48.—The two chief classes of igneous rocks : upper curve, alkali-content of alkaline series ; lower curve, of calc-alkaline series.

Of late years attempts have been made in some quarters to confuse the issue by the introduction of a third rock-group, called the *spilites*. The writer believes that there is no justification for this, since the only difference that appears to be claimed as existing between spilites and the true alkaline rocks of this classification is that in the former soda is in considerable excess of potash. This is the case also with many soda-granites, syenites and especially nepheline syenites, which even the most ardent supporters of the Spilitic Suite have not ventured to claim as belonging to it.

Soon after the existence of this double rock series was recognized, it was pointed out by Harker [1] that a connection could be traced between the chemico-mineralogical character of the igneous rocks of a given area and the type of crust-movement controlling the eruption or intrusion of the magma. The highly alkaline rock-types were seen to be mainly associated with structures of a simple kind ; block-faulting and uplift or subsidence of the crust due to vertical movements with little or no horizontal component : structures of this kind are most conspicuous around the Atlantic coast-lines, hence in a general way the alkaline rocks are called the Atlantic Suite. On the other hand calc-alkaline rocks are chiefly found in association with regions of intense folding due to tangential movements of the crust, such as are so conspicuously developed along the sea-board of eastern Asia and the whole western side of the American continent from Cape Horn to Alaska. They are therefore called the Pacific Suite. The so-called Spilitic Suite is said to accompany depression of the floor of the deep sea, but many submarine lavas do not conform at all to this type.

An interesting and striking application of the connection between the chemical characters of rocks and types of crust-movement is to be found in the case of the Tertiary chain of the Alps and Carpathians, which shows a clear instance of a thrust towards the north and north-east ; i.e. outwards. In south Germany, Bohemia, Moravia, etc., in front of the chain, the volcanic rocks are alkaline ; in Hungary and Transylvania, in the sunken region behind the chain, they are calc-alkaline. Again in the Rockies, a chain strongly folded towards the east, there is a great development of calc-alkaline rocks, both intrusive and extrusive, whereas in the plateau region east of the Rockies, are many examples of highly alkaline rocks. The intrusions accompanying the formation of the great rift valley of the Kristiania Fjord are very alkaline types, and the same is true of many of the great volcanoes of the African Rift Valley (Kenya and others). Among the Tertiary igneous rocks of the British Isles and of the Brito-Arctic region generally is to be seen much block-faulting, with rocks of alkaline affinities : where local patches of tangential disturbances are to be seen there the rocks are more dominantly calc-alkaline ; also the later rocks developed in the Late Carboniferous rift valley of Central Scotland include many very markedly alkaline types, whereas the earlier Devonian eruptions, which were concomitants of strong tangential thrusts, are conspicuously calc-alkaline.

It is not proposed in this book to discuss the detailed classification and nomenclature of the igneous rocks. Full information will be found in almost any modern text-book of geology and various special treatises.[1] In what follows it will be assumed that the student is acquainted with the meaning of the ordinary petrographical terms in common use, both classificatory names and those descriptive of structures.

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[1] Harker, A., *Science Progress*, vol. vi, 1896, pp. 12–33. *The Natural History of Igneous Rocks*, London, 1909, pp. 90–100.

Rock Structures and Textures. The igneous rocks in general show a wide range of variation in the mutual relations of their component parts, leading to great differences in size of grain and general appearance. These variations are frequently described as structures, but for most of them the word texture is better. In the first place, some rocks are entirely glassy, while the majority are more or less crystalline, many being wholly so. All true plutonic rocks are entirely crystalline (holocrystalline) while hypabyssal and especially volcanic rocks often show some amount of glass, which is usually the last portion to solidify. Some of the most conspicuous of these textural variations are determined by the absolute and relative sizes of the component crystals, by the time-relations of one mineral to another and by the space-relations of different crystals or groups of crystals. Most of these variations depend on physical conditions prevailing during crystallization. Some of the more important of them will here be discussed from the physico-chemical point of view.

Many of these points can be well illustrated by reference to the textures of the volcanic (effusive) rocks. Here we see every gradation from purely glassy to holocrystalline types, the differences being largely controlled by rate of cooling, but also to some extent by chemical composition, since it seems clear that, other things being equal, a highly siliceous lava is more prone to solidify as a glass than one with a lower silica percentage. This fact is clearly correlated with the greater viscosity of highly siliceous melts. An acid lava-flow is often glassy throughout (obsidian) whereas in a basalt the purely glassy product is often confined to a superficial layer of scoria, the lower part of the flow being crystalline, sometimes with a little interstitial glass.

The differences of texture observable in the lavas largely depend on whether at the time of eruption the magma was still wholly liquid, or already contained crystals of one or more minerals. In the first-named case the texture of the solidified rock will be uniform, either wholly glassy or microcrystalline and of even grain, with or without steam cavities, which may either remain empty, as in pumice and other vesicular types, or may later be filled up by deposition of secondary minerals, often zeolites, as in the amygdaloidal types. It is hardly necessary to discuss at this stage the laws governing the solidification of silicate melts as glass or crystal aggregates ; these have already been dealt with in the introductory chapters, but the infilling of the gas-cavities in vesicular rocks is a subject of much interest and worthy of some consideration here.

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[1] Hatch and Wells, *The Petrology of the Igneous Rocks*, 8th edition. Allen & Unwin, 1926.

Amygdaloidal Structure and the Infilling of Vesicles. In its essential features the formation of gas cavities in lavas is exactly the same as in artificial slags. The cavities are mostly due to steam, with perhaps some other volatile constituents, whose nature is not of much importance, since they condense or escape at an early stage, and have little or nothing to do with the later infillings of the cavity. These cavities may be of any size whatever, from microscopic dimensions up to quite large caverns : sometimes they remain empty, as in pumice, but more often they are filled up by later minerals. These minerals show a good deal of variation. Fairly common species are calcite, and silica in various forms, sometimes quartz, but much more often some form of chalcedonic or opaline hydrated silica. Most of the Iceland Spar, as used in the construction of nicol prisms and other forms of optical apparatus has been obtained from a single immense vesicle in a basalt in Iceland. Among the siliceous infillings the variety is endless, giving rise to many kinds of agates, onyx and other forms of silica, often showing a banded structure. This in itself is a large subject and has given rise to a very considerable literature, but it cannot be dealt with here.[1]

However undoubtedly the most characteristic of all vesicular infillings are the minerals of the zeolite group, which are found specially in basalts (e.g. N.E. Ireland, Iceland, and the Western Ghâts near Poona). The zeolites form a large and complicated mineral series showing many points of interest, both chemical and crystallographic. They are all essentially hydrated aluminosilicates, showing much analogy to the felspars, from which they differ, from the chemical standpoint, mainly in the presence of a large proportion of very loosely held water of crystallization. In fact in many cases it has been shown that the amount of water present is a continuous function of the temperature and pressure. Now to put the matter briefly, these zeolites possess exactly the composition that we should expect to find in the last residue of a crystallizing magma, and there is little doubt that the infilling of the vesicles with zeolites is directly due to magmatic solutions derived from the same source as the lavas themselves. Therefore, although showing very different structures they are in reality closely allied to the pegmatites of the plutonic rocks. A similar argument applies exactly to the siliceous infillings before referred to, but it is doubtful how far this can be applied to calcite. Independent evidence also shows that the infilling of the vesicles has in some cases taken place very soon after eruption.[1]

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[1] See especially Liesegang, *Geologische Diffusionen*, Dresden. Steinkopff, 1913.

In most cases the cavities, whether empty or filled, are of a more or less spherical or ellipsoidal form, as would naturally be expected in the case of gas-bubbles. However in certain lavas known as pipe-amygdaloids there are found peculiar structures, that need a special explanation. The pipe-amygdaloids of the Drakensberg in South Africa or of the basalt plateau of N.E. Ireland show curious tube-like, often branching structures, often many inches long and generally arranged more or less vertically at the bottom of a flow, and filled with the usual calcite, silica or zeolites. It is believed that these lavas flowed when hot over damp ground and that the pipes are due to evolution of steam from water in the soil, the infilling having afterwards followed the usual course.

Porphyritic Texture. One of the most notable features of a large number of igneous rock-types is the occurrence of what is known as *porphyritic texture*. This means that crystals of one or more minerals are notably larger and better formed than the rest. In some cases they may be embedded in a glassy base, while in other instances the ground-mass may be very finely crystalline (felsitic). In other types the ground-mass is comparatively coarse, but always consisting of crystals smaller and less well formed than the so-called *phenocrysts*. The main point of the term is that one set of crystals stand out clearly and visibly from the rest of the rock.[2]

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[1] Harker, *The Tertiary Igneous Rocks of Skye*, 1903, p. 45. Brögger (*Zeits. f. Kryst.*, vol. xvi, 1890) describes formation of zeolites as a late phase of pneumatolysis.

[2] The history of the terms porphyritic and its derivative porphyry is most interesting and instructive ; it happened that a certain ornamental stone of a purple colour, very popular in classical and mediæval times, possessed this texture. It was named (quite reasonably) porphyrios. In the middle of the nineteenth century certain systematic petrographers proceeded to extend this nomenclature. The argument appears to have been as follows : porphyrios (German Porphyr) means purple stone : therefore " phyr " means stone. Hence this term can be extended to other rock types, e.g. vitro-phyr, a glassy rock, granophyr, a granular rock, and so on. But perhaps the most barbarous construction of all is felsophyr (German fels, a rock). This was supposed to connote a rock of very fine, irresolvable texture. Actually, of course, the word conveys no information at all, except as to its proposer's complete ignorance of classical languages. However, these painful incidents in the history of petrography may now be regarded as closed. The term porphyry has established its place as a useful descriptive term and may be retained in spite of the absurdity of its origin.

Now the obvious explanation of this type of texture is that the rock solidified in two stages, one under conditions that favoured the growth of large crystals and the other leading to rapid chilling and fine texture or even glass-formation. In many cases this is undoubtedly true. At the time of eruption or intrusion the magma contained ready-made crystals of considerable size and the liquid solidified round them. Some rocks, however, and especially plutonic rocks, show features that make it difficult to accept this explanation, and it seems quite clear that more than one cause must be invoked. Furthermore it is possible to explain on theoretical grounds the occurrence of well-developed crystals of one or more minerals in a finer ground mass, without making any assumptions as to physical changes during solidification.

(*a*) It has already been pointed out in general terms that in a mixed system of two or more components eutectic relations hold: the components in excess of the eutectic ratio first separate, while the eutectic residue finally solidifies as an aggregate, usually of fine texture and even grain, sometimes, but not always, showing graphic relations. This accounts for one type of porphyritic structure without any discontinuous change of conditions. It is probably applicable to many cases where the large crystals (phenocrysts) show no signs of corrosion or resorption, as hereafter described. It is of course obvious that if the system consists of n components, regarded as mineral molecules, e.g. quartz, felspar, mica, etc., there may be phenocrysts of $(n - 1)$ minerals. Further, the order of appearance of the minerals, and therefore in all probability their relative sizes, will depend on their concentration in the magma. It is probable that this explanation can be applied to many types of quartz-porphyry and other rocks of comparatively simple mineral composition, where the phenocrysts are mainly or entirely quartz or felspar or both.

(*b*) It is a matter of common observation that in many porphyritic rocks the phenocrysts show a more or less corroded appearance, indicating partial solution after crystallization: sometimes again a phenocryst may contain inclusions of foreign matter, usually minerals like those of the ground mass arranged in a zonary fashion, as if growth had been renewed after corrosion and partial re-solution. It is noticeable also that in some rocks phenocrysts of one mineral may be corroded, while another is unaffected—e.g. in some Tertiary trachytes and andesites from the Rhine district biotite and hornblende are very badly corroded, while augite is quite sharp and unaffected. These phenomena, which are known as resorption, can be explained on physico-chemical grounds as follows:

In the *pt* diagram (Fig. 49) let A, B and C represent the freezing-point curves of three minerals, whose freezing points are as usual raised by pressure. The point *x* will then represent the state of a magma before eruption or intrusion; as cooling proceeds the temperature falls from *x* to *y*: at *y* the solution is saturated for the mineral *C*, which begins to crystallize, while similarly at *z* the mineral *B* will begin to form. At such a point as *v* then there will be phenocrysts of *C* and *B* suspended in liquid. Let it be supposed that at the point of time represented by *v* the magma is erupted as a surface flow: this is mathematically equivalent to an abrupt movement of the system along the isotherm *vw*, since the temperature would probably remain approximately constant during the eruption. At *w* however the mineral *B* is above its melting-point

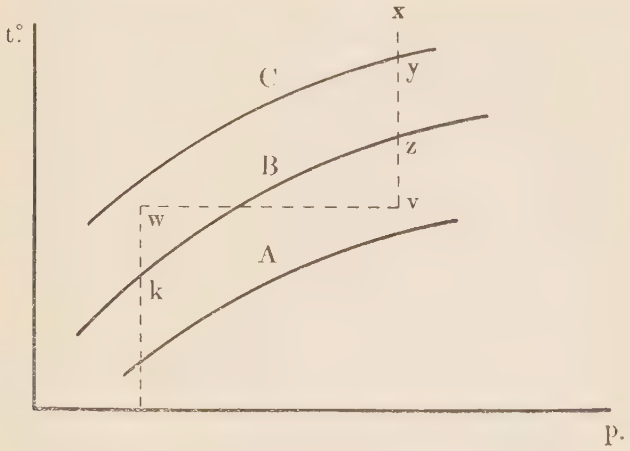

Fig. 49.—Freezing-point curves of three minerals, to show relation of resorption to change of pressure during extrusion.

curve and therefore unstable: it will be more or less completely dissolved in the liquid, or resorbed. The mineral *C* is still within its field of stability in contact with liquid, and is not resorbed. From the point *w* the temperature will continue to fall along the vertical line, and at *k* the freezing-point curve of *B* is again intersected, so that the growth of the crystals, if any remain, will be renewed. The continuity of growth, however, is usually not perfect and the gap is made visible by a zonary shell of inclusions. The mineral *A* was still completely soluble in the liquid at the time of eruption and its crystallization belongs only to the later stage. Hence *B* is resorbed, *A* and *C* are not.

Hence it appears that the occurrence of resorption, and especially of differential resorption, affords strong evidence of a change of physical conditions during cooling.

A zonary structure in minerals of the type here described must be carefully distinguished from the other type of zonary structure in mixed crystals with complete isomorphism, as explained by the principle of continuous reaction (see p. 31). This involves no sudden discontinuity of conditions and in such zoned crystals, e.g. plagioclase felspars, the structure is often only brought out by polarized light, whereas true resorption is often visible to the naked eye.

(*c*) We must now consider briefly the possible origin of porphyritic structure as often seen for example in plutonic rocks, when a discontinuous change of pressure is excluded. In many granites porphyritic structure is found on a very large scale, the phenocrysts being sometimes as much as 6 inches across, e.g. the Land's End granite, Cornwall, while phenocrysts of 1 to 2 inches are very common. The phenocrysts of deep-seated granites often show certain features suggesting that their formation may be due to a cause somewhat different from those outlined above. Besides the occurrence of zonary lines of inclusions, as above described, it is often to be observed that the outlines of the crystals are somewhat irregular and indefinite, interlocking more or less with the granular aggregate of the ground-mass. Such phenocrysts in many cases probably represent the excess of the mineral over the eutectic ratio, having continued their growth to some extent after the eutectic point was reached. A very common case also is to be seen where large felspar phenocrysts show at their edges a gradual transition to a graphic undergrowth of felspar and quartz, which constitutes also the whole or the greater part of the ground-mass. Such instances can doubtless be referred with safety to the eutectic principle. It is believed, however, by many writers that graphic structure is by no means invariably found in eutectic mixtures, and that many granites of normal granular structure correspond essentially to a eutectic composition.

The formation of many examples of somewhat vague and irregular phenocrysts has been explained on physico-chemical grounds on the basis of a rule first enunciated by Ostwald, namely, that in a saturated solution maintained for a long time at a temperature at or just below the freezing point crystals which for any reason have become larger than the average tend to grow still further at the expense of smaller ones.

Some plutonic rocks show a kind of pseudo-porphyritic structure, in that it is often impossible to draw a clear distinction between the phenocrysts and the crystals of the ground-mass in regard to size, crystals of every grade of dimensions forming a complete transition. It is probable that this can be correlated with a gradual escape of the so-called mineralizers from the magma, involving an increase in viscosity and the consequent setting up of new centres of crystallization at smaller distance-intervals, and it is even possible that the natural increase of viscosity on cooling, without change of composition, might show itself in a more or less abrupt diminution in size of crystals.

With regard to the general prevalence of porphyritic structure in the different rock-types it is difficult to generalize. It is common in volcanic (eruptive) rocks of all kinds and is specially characteristic of the more acid intrusives (whence the names, quartz-porphyry, porphyry, and porphyrite commonly applied to these groups). In the dolerites it is less common, though sometimes well developed. Among the plutonic rocks a decided porphyritic texture can only be said to be really common in the granites : in the diorites, gabbros and ultrabasic types it is much more rare. It is doubtful, however, whether this really means anything more than that basic plutonic rocks are much less common than acid ones, which is a well-known fact.

The Cooling of a Granitic Magma. As an example of the general processes involved in the solidification of an igneous intrusion we may take the case of a large granite laccolith, as being in some respects the most representative and certainly the commonest type. The earlier stages are quite simple and do not need minute description, as most of the principles have been already discussed. First of all the so-called accessory minerals separate in the order of their solubility in the magma, for the most part apparently at pretty high temperatures. It is a point that cannot be too strongly emphasized that the separation of a mineral from a melt depends on its solubility in the melt and *not* on its absolute freezing point in air. Then as cooling goes on the magma becomes saturated for one of the principal components, say biotite or hornblende. Saturation will probably take place earliest at the margin of the laccolith, generally at the top, and there may be a certain amount of diffusion, to restore equilibrium, leading to a marginal concentration of the ferromagnesian mineral (see also p. 107). Next will come separation of the felspars and finally of quartz, or if the magma is very acid some quartz in excess of the eutectic ratio will come out at an earlier stage. The possible formation of porphyritic crystals need not here be discussed again. So far the matter is very simple : however it is clear that most granitic magmas contain also a good deal of water and other volatile constituents, such as fluorine and boron. These substances have important effects in two ways. In the first place they lower the freezing points of the more abundant minerals, and secondly they tend to keep the residual liquid very mobile : in fact in both ways they act as a flux. (A highly siliceous melt without any flux is always very viscous, as is shown by experimental work on mineral formation, and by ordinary smelting practice.) Along with these fluxing materials there are often concentrated in the last residue of the magma other less abundant constituents, such as lithium and beryllium, both elements of very low atomic weight, and also certain of the heavy metals, for example tin, tungsten, copper, lead and zinc. It is an interesting point, and one of much practical importance in the study of the origin of ore-deposits, that the accessory constituents of the magma can be divided pretty clearly into two groups, which separate respectively very early or very late in the cooling. Thus zircon, sphene and magnetite crystallize very early, while most of the metals and rare earths come out in the very last stages. This is probably to be correlated with their power of forming volatile compounds with fluorine, boron, etc.

The last residue of a normal granitic magma, then, consists of a highly siliceous and watery liquid, very mobile and carrying in solution many peculiar mineral molecules. The vapour pressure of such a solution is naturally very high, owing to the presence of superheated water, probably above its critical point, and other gases. Now the granite of earlier solidification, on further cooling, must contract in volume, giving rise to open joints, and affording a passage for the high-pressure fluids within. These fluids therefore pass outwards through the granite and often fill joints in the rocks around, thus forming veins and dykes, which are characterized by very coarse texture and often by the presence of uncommon minerals. These constitute the rock types known to petrographers as *pegmatites*, while the most highly siliceous types form *quartz-veins*. There has been in the past much unprofitable controversy as to whether pegmatites and quartz-veins are of igneous or of aqueous origin. As just shown both views are correct and the whole thing is purely a matter of degree. In many cases veins which everybody would agree to call pegmatites have been traced laterally, with gradual mineralogical change, into pure quartz-veins. Many of the gold-bearing quartz-veins contain also a little felspar or mica, and it is clear that the whole process of vein-formation is in effect a matter of fractional crystallization, the last fraction containing nothing but silica and water. The last term in this series is afforded by some of the geysers and hot springs that now deposit siliceous sinter.

The most notable characteristics of the pegmatites are therefore the common presence of rare minerals, the great size of some of their component crystals, and another point not yet mentioned, the common occurrence of graphic intergrowths of minerals, more especially quartz and felspar. The last feature is easy to understand when it is considered that the composition of the last residue of a complex solution undergoing crystallization must of necessity approach to or attain the eutectic ratio, so that two or more minerals are crystallizing together.

Unfortunately space will not permit of a further description of pegmatites, which present many points of mineralogical interest, while many of them are of great practical importance as sources of ore-minerals, mica, rare earths, cryolite and other technical products of great commercial value. Quartz veins also yield a large part of the gold output of the world.

Besides the coarse-grained segregations just described there are to be seen in most granites also veins of a much finer texture than the average, and usually of a paler colour. These are called *aplite.* As a rule the aplites are somewhat more acid than the normal granite and they sometimes contain garnet and other less common minerals. In origin the aplites are essentially similar to the pegmatites, the difference lying mainly in the structure. They represent portions of the residual liquid from which the mineralizers or fluxes have escaped so that the liquid was very viscous. Consequently numerous centres of crystallization are set up and the individual crystals remain small. Aplites do not often contain minerals of technical importance.

Differentiation in Igneous Magmas. As already mentioned igneous rocks show a certain fairly wide though limited variation in chemical and mineralogical composition. This range of variation expresses itself in the field in two chief ways. In the simplest case there is to be seen within the limits of a single rock unit (laccolith, dyke or sill) a variation in composition, sometimes in sharply bounded masses, sometimes showing gradations in space and transitional types. In many instances it is quite clear that this heterogeneity has been produced as a result of definite processes occurring within one originally homogeneous mass, but not accompanied by any mechanical process of separation. A related phenomenon is shown by the occurrence in certain areas of independent rock masses, which evidently arrived separately in their present position, but nevertheless carry indisputable evidence of relationship and origin from a common source. Both these groups can be explained as due to essentially similar causes, differing only in the final degree of separation, in reality a somewhat unimportant detail, of no true genetic significance. This general phenomenon, namely, the formation of heterogeneous rock-masses from originally homogeneous magma is summed up under the general name of *differentiation.*[1]

Confining attention for the present to differentiation in intrusive rocks, it is clear that two types can be recognized, distinct in their effects, though probably similar in their causes, namely differentiation before intrusion, and differentiation after intrusion.

During the last thirty years or so there has been a great deal of controversy as to the nature of the processes leading to these results, and the question cannot yet be regarded as settled. In all probability most of the explanations now put forward are true in certain cases, though some of the earlier physical theories are now believed to be inadequate.[2]

Although as has been seen differentiation of igneous magmas shows itself in the field in two different ways, firstly in the existence of related but physically independent rock-masses and secondly in the production of heterogeneity in a single rock-mass, the deep-magmatic and laccolithic types of Brögger, nevertheless there is every reason to believe that the same fundamental causes have been at work in both instances, the difference of result being more or less accidental and subsidiary. It is necessary now to summarize as briefly as possible the explanations that have been put forward to account for differentiation.

When this subject first came under discussion about 40 years ago various more or less abstruse physical explanations were suggested, such as Soret's principle and the theorem of Gouy and Chaperon, as well as magnetic concentration: these ideas have not stood the test of quantitative application and need not be considered further.

Turning at once to more modern ideas, one point in need of early consideration is the following: it is a matter of observation that in a great number of cases an originally homogeneous magma appears to have split into two fractions, acid and basic respectively. The extreme case of this is the conception, long ago originated by Bunsen and others, and now strongly supported by Daly, of the two primitive earth magmas, granitic and basaltic, an idea which is now so prevalent in the form of the Sal and Sima of Suess and the

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[1] This is a rather unfortunate term, owing to its mathematical connotation, but it has come to stay, being now universally employed in all civilized languages in this special sense.

[2] Although in recent years the discussion of the general subject of differentiation has been largely carried on in America, Scandinavia and Germany, it is well to remember that much of the earliest field-work bearing on the subject and many of the earlier theoretical discussions concerned British rocks. Special mention may be made of the work of Harker and Marr at Shap, Harker at Carrock Fell, Teall in the Cheviots, and Dakyns and Teall at Garabal Hill. These observations were largely the ground-work of the later theoretical superstructure.

Wegener hypothesis. This idea rests either explicitly or implicitly on the fundamental assumption of limited miscibility. This raises a difficult problem. As a result of all the numerous experimental and synthetic researches of the last few years it may be said that under artificial conditions all silicate solutions appear to be completely miscible in all proportions ; there is no experimental evidence at all in support of the theory that a silicate melt tends to split into two conjugate solutions. Nevertheless many of the facts of nature indicate pretty clearly that something of the sort does occur. Unfortunately we have no data as to the relative sizes of the different fractions that appear to be formed, and without such information it is impossible to draw any definite conclusions. It is obvious that the separation of a basic fraction amounting to perhaps 0·0001 of the total magma is not at all the same thing as the separation of a magma into two equal halves, and may be due to entirely different causes. The separation of small fractions can be explained in a good many different ways, but the formation of two more or less equally important world-magmas is a proposition of a different order, and much more difficult to account for. Nevertheless it is a fact that the dominant rock-types of the world are granite and basalt, using the terms in a broad sense, or to put the matter in even more general terms, the commonest igneous rocks are acid intrusives and basic lavas. The intrusive and extrusive character of these typical magmas is doubtless correlated with their different degrees of viscosity, but this bears no necessary relation to their primary differentiation.

Causes of Differentiation. Turning to the small scale phenomena of differentiation, as above alluded to, it may be said that from the copious discussions of the subject in recent years there have emerged at least five different explanations, each of which is probably applicable in particular cases. These may be conveniently summed up under the following headings :

(1) Diffusion to the cooling-surfaces before and during crystallization.

(2) Sinking of crystals by gravity during crystallization.

(3) Squeezing out of the liquid phase from a partially crystallized magma.

(4) Separation of two immiscible liquid phases.

(5) Assimilation of country rock.

Each of these must be described as briefly as possible : for full details of the evidence available reference must be made to the original sources.

(1) *Differentiation by Diffusion during Crystallization.* The classical instance of this type of differentiation is the gabbro of

Carrock Fell, as described by Harker.[1] Here a large, steeply inclined laccolith or thick sill shows a strong concentration of basic minerals, ilmenite and pyroxene, on both margins, and a corresponding enrichment of the middle part with silica, so that the silica percentage varies continuously from 33 to 59. The theory here is as follows : when crystallization began at the cooling surfaces the least soluble mineral, ilmenite, separated first as crystals ; this separation disturbed the equilibrium of the solution and there was a consequent diffusion of liquid ilmenite molecules towards the margins. These in their turn began to crystallize as temperature fell, thus draining off ilmenite molecules from the central parts. On further fall of temperature the limit of saturation for pyroxene was reached, this mineral in its turn becoming concentrated, though to a somewhat less degree. After a while the increasing viscosity of the now more siliceous solution would put a stop to further diffusion, and even at the centre some ilmenite and pyroxene still remain, but the composition of the middle part was acid enough to entail the formation of some quartz.

This is of course an unusually well-marked case, but something of the sort can be seen to a greater or less degree in nearly all fairly large intrusions, and it occurs in some quite small sills and even in narrow dykes. This kind of differentiation is evidently independent of gravity and may even lead to concentration of heavy minerals on the top of an intrusion, provided the magma is sufficiently viscous to prevent sinking of the crystals.

(2) *Gravity-differentiation.* This theory, which is strongly supported by Bowen and other American petrologists, is so simple as to be almost self-explanatory. The theory depends on the observational fact that rock-forming minerals have a higher density in the crystalline than in the liquid form and therefore tend to sink on freezing. Further, the minerals that separate first in the normal empirical order of crystallization are as a rule heavier than the average of the rock, thus accentuating this tendency. The facts of field observation in support of the theory consist mainly in the occurrence in many large intrusions of a basic or ultrabasic layer at the bottom and an acid layer at the top, with usually a complete gradation between them : e.g. the Palisade Traps of New York and New Jersey show a transition from an olivine-dolerite at the bottom to a rock of granitic composition at the top. The most weighty objection urged against this theory, especially by Harker, is that the viscosity of silicate melts is so great that gravity-sinking would very soon stop, even if it once started. In this connection the concentration of ilmenite at the hanging-wall at Carrock Fell is instructive.

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[1] Harker, *Quart. Journ. Geol. Soc.*, vol. l, 1894, pp. 311–336.

(3) *Differentiation by squeezing during Crystallization.* This theory is of course only applicable in instances where well-marked crust-movements have occurred during crystallization. At one stage a partially solidified magma may be compared, according to Harker, to a sponge full of water, the earlier-formed crystals building a kind of lattice with its interstices full of an acid residue. This residual liquid when squeezed out penetrates the surrounding rocks in front of the advancing earth wave, leading to the formation of pegmatite veins and the so-called *lit-par-lit* injection of granitic material into schists or stratified sediments. This idea was long ago applied by Barrow to the pegmatitic injections of the south-eastern Highlands.[1] The part of the magma remaining in place will of course be more basic than the average of the original magma, but in the known cases the composition still seems to be mainly granite. Probably the proportion squeezed out is not very large.

(4) *Separation of Immiscible Liquid Phases.* The theoretical foundation of this type of differentiation is simply the common practice of copper matte smelting and it is probably only applicable to the separation of sulphides from silicates. Many of the great pyrite ore-bodies of the world are undoubtedly intrusive (e.g. Rorös and Sulitjelma, Norway; probably Rio Tinto, Spain; and the great nickeliferous pyrrhotite ore-bodies of Sudbury, Ontario). The researches of Vogt,[2] as well as smelting practice, show that silicates and sulphides possess very limited mutual solubility and must separate into two conjugate solutions, which will either solidify in place, the heavier below; or they may be drawn off and separately injected elsewhere. This type of differentiation may be said to be the foundation of industrial chemistry, since such pyrite bodies are the chief source of sulphuric acid. The physico-chemical theory of this type of differentiation is fully discussed in Chapter II, p. 35.

(5) *Assimilation of Country Rock.* It is a fact well known to all geologists that igneous rocks often contain obvious blocks of the wall-rock (xenoliths) and that in many instances it is possible to trace every gradation from such scarcely-altered blocks to heterogeneous but apparently completely re-crystallized patches in the intrusion. Such inclusions often show themselves merely by the presence of crystals of andalusite, cordierite, corundum, lime-silicates, or some other non-igneous mineral. It is suggested especially by Daly[3] that this type of assimilation is an important factor in differentiation. For the actual process of inclusion Daly suggests the term *overhand stoping,* a term used by miners to describe

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[1] Barrow, *Quart. Jour. Geol. Soc.*, vol. xlix, 1893, pp. 330–356.

[2] Vogt, *Die Sulfid-Silikatschmelzlösungen.* Kristiania, 1919.

[3] Daly, *Igneous Rocks and their Origins.* New York, 1914, especially Chapters X and XI.

the process of breaking down a vein by pulling down the roof of a level. Just in the same way the magma is supposed to pull down the roof of its basin, the material being then partly melted down, or partly sinking in the magma. Daly attributes specially important effects to the fluxing action of limestone or dolomite swallowed up in this way ; these then partly displace the alkalis of the silicate solution, which separate off as highly alkaline fractions (syenitic and trachytic differentiates). Some highly alkaline rocks containing original calcite and dolomite have recently been found in Norway, a strong support for this theory.[1]

The differentiation of igneous magmas has for long been a favourite subject for speculation among theoretical geologists, but it has recently acquired great practical importance from its bearing on the origin of ore-deposits. The earlier theories of the origin of metalliferous veins by deposition from meteoric waters circulating in the upper crust, though still lingering in some quarters, may now be regarded as definitely superseded, in the light of recent work, especially in America, and it is now being increasingly recognized that the vast majority of primary ore-deposits really belong to the category of after-effects of igneous activity. The ore-bearing solutions are of essentially similar nature to those concerned in the formation of pegmatites and in the phenomena of pneumatolysis and even the distinction lately drawn by many writers between magmatic and hydrothermal solutions has broken down.[2] Every gradation both in time and space can be traced from the pegmatitic aggregations of the plutonic magmas, through dykes and metalliferous veins with ores of tin, copper, lead and zinc to the gold-bearing quartz veins and the barren quartz, barytes and calcite veins found in nearly all regions where vulcanicity, crust disturbance and metamorphism have occurred. A common quartz vein, just as much as a hot mineral spring, is to be regarded as a final product of the differentiation of an igneous magma. In some instances such veins may be of secondary origin, but when primary their magmatic origin is clear.

Examples of Differentiated Rock-Series. In a work of this character it is impossible to devote much space to the description of actual instances of differentiation, but one or two cases may be briefly referred to in illustration of general principles. The number of instances now described in detail is very great, and they naturally show much variation, but in a general way they can be ranged under the general categories of differentiation before intrusion, and differentiation after intrusion. However it must be understood that in one and the same area both types may be and often are found.

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[1] Brögger, *Die Eruptivgesteine des Kristianiagebietes*, iv. *Das Fengebiet.* Kristiania, 1920. Summary by Dr. C. E. Tilley, *Geol. Mag.*, vol. lviii, 1921, pp. 549–554. For an adverse criticism of Brögger's views, see Bowen, *Amer., Jour. Sci.*, vol. viii, 1924, pp. 1–11.

[2] Rastall, *Trans. Faraday Soc.*, vol. xx, 1925, pp. 459–460.

The first category, wherein the main differentiation occurs at a great depth before emplacement of the rock in its present position, leads normally to the occurrence in a given area of a series of separate intrusions, which may be contiguous or some distance apart. They will necessarily show some character or aggregate of characters, chemical or mineralogical, indicating a genetic relationship, and if the separate intrusions are numerous they may form a series. It is usually found that the most basic intrusion came first, followed by others in the order of increasing acidity ; in a calcic province the sequence will be peridotite, gabbro, diorite, tonalite, granite ; in an alkaline province peridotite, alkali-gabbro, syenite, soda-granite. But all the members need not be, and often are not, present. An exceedingly good example of an alkaline series is afforded by the Devonian intrusions of the Kristiania region which will be briefly described later. First however it must be pointed out that each of such separate (laccolithic) intrusions may itself undergo a secondary differentiation after intrusion, and that such differentiation may take two distinct forms : either the formation of heterogeneous phases, marginal or basal, due to diffusion-crystallization or to gravity-sinking ; or, secondly, the separation of fractions of the magma with separate injection as dykes or sills. All these types are illustrated by the Kristiania series, where we have a sequence of independent laccoliths, ranging from basic to acid, each with marginal modifications and its own series of dykes.

Another important point in connection with the relationship of dyke rocks to plutonic intrusions is this : such dykes may be the same in composition as the parent laccolithic magma, or they may themselves have undergone further differentiation. In many instances field-relations show clearly that two or even more types of dyke-rock are derived from one plutonic mass. The elvan dykes so common in Cornwall (quartz-porphyries, usually with tourmaline) are an instance of the first kind : they are all granitic in composition, and essentially similar to the granites from which they have been separated. This kind of thing is exceedingly common around intrusions of all compositions and further instances need not be given.

The second type, the double series of dykes, is well illustrated by two British examples described many years ago. Around the granite of the Cheviot Hills, of Old Red Sandstone age and calcic affinities, are a number of radiating dykes, some of which are a fairly acid-quartz-porphyry, while others consist of a rather basic mica-porphyrite.[1] Again the granite of Shap in Westmorland is accompanied by dykes of quartz-porphyry and mica-lamprophyre. The last-named are very basic, but their derivation from the granite magma is shown by the sporadic occurrence in them of large phenocrysts of red felspar, like those of the granite, often much corroded ;[1] some of these are found many miles from Shap, intruded into the Lower Palæozoic rocks of Edenside.

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[1] Teall, *Geol. Mag.*, 1885, pp. 106–121.

The physico-chemical relations of such differentiated dykes may be looked at in the following way ; since each pair are derived from a single magma they are called *complementary* dykes.

We have seen that the composition of a given magma can be represented in a diagram by plotting some one constituent on the sum of a set of constituents, usually total alkalies against silica :—

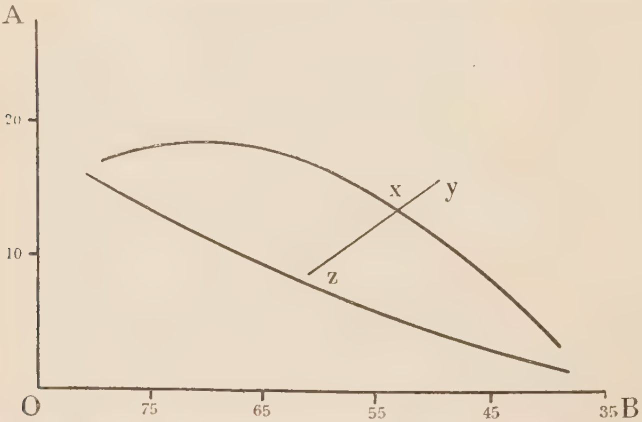

Fig. 50.—Diagram to show how the differentiation product of an alkaline magma may approach in composition to a calc-alkaline rock. (Compare Fig. 47.)

Let x in Fig. 50 represent the composition of an undifferentiated magma : if such a magma is now split into two fractions the compositions of the fractions will be represented by two points, y and z, which must necessarily lie in one straight line with x, and the distances yx and xz will be inversely proportional to the masses of the two fractions : hence it follows that the more the differentiate differs from the initial magma, the less can be the amount of it. This is another expression of the fact that extreme rock-types are never abundant. In such a diagram it is clear that theoretically at any rate the line xyz may be inclined at any angle ; hence very varied rock-types may be produced from one magma and a little consideration will show that a differentiate of an alkaline magma may be a rock low in alkalies, i.e. apparently belonging to the Calcic Suite and vice-versa. It is perhaps hardly necessary to state that for the purposes of this argument assimilation of foreign material as a cause of differentiation must be excluded: the idea is only applicable if the *total* composition of the system remains unchanged.

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[1] Harker and Marr, *Quart. Jour. Geol. Soc.*, vol. xlvii, 1891, pp. 266–325.

In the Kristiania district we have in one area and in one connected series rocks showing all these types of differentiation. Stated in the most simple terms the relations are as follows: first, there is a series of laccoliths of plutonic rocks ranging from olivine-gabbro (essexite) through nepheline-syenite and syenite to granite; secondly each of these laccoliths shows marginal modifications, usually more basic, and each is accompanied by normal dykes of similar composition and by a set of complementary differentiated dykes. For details the original memoirs[1] or some textbook of petrology must be consulted, but the main points may be conveniently summed up in the following table.

Plutonic.	Undifferentiated Dykes.	Differentiated Dyke-pairs.
Soda-granite (Ekerite)		
Nordmarkite (quartz-syenite)	quartz-rhomb porphyry	
Laurvikite (syenite)	rhomb-porphyry	
Laurdalite (nepheline-syenite)	nepheline-rhomb-porphyry	
Essexite (olivine-gabbro)		bostonite camptonite

Of all these rock-types nordmarkite, a quartz-syenite with arfvedsonite and aegirine is the commonest, and may be regarded as the primary magma from which the others are derived. All types are characterized by high soda-content and even in the granite soda is dominant over potash.

Differentiation and Ore-deposits. As before stated, the most important practical application of modern theories of magmatic differentiation is in connection with the origin of ore-deposits. Recent detailed studies from the petrological point of view have thrown a flood of light on the origin and nature of the occurrences of the metals and their genetic connection with different rock-types, thus facilitating not only the exploitation of known deposits, but also helping in the discovery of new ones. In fact petrology is the foundation of scientific prospecting.

The first point, now fully established, is that a perfectly regular and complete transition exists from normal igneous intrusions, through various differentiated facies (pegmatites, aplites, etc.) to the different types of ore-bearing veins of more or less complex mineral composition. Secondly, the so-called contact and replacement ore-deposits are of essentially the same nature as the products of what is commonly called pneumatolytic or metasomatic metamorphism. It must of course be understood that ore-deposits like all other rocks, perhaps even to a higher degree than most rocks, are subject to various secondary changes : these effects are not here discussed, attention being confined to primary types.

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[1] Brögger, *Die Eruptivgesteine des Kristianiagebietes*, Parts I–III. Kristiania, 189, 1894–95–98.

As a result of recent generalized studies, founded on detailed examination of a large number of cases it has now been established that primary ore-deposit (mineralization) on a large scale can be traced to igneous activity, generally to deep-seated intrusion, though in certain cases the association of certain metals with surface eruptions is also clear. Large scale deposits of particular metals are also associated with particular rock-types, while around any given metal-bearing intrusion it is usually possible to trace a definite zonary succession of ores, this regular arrangement in space being due to simple and easily determinable physico-chemical causes.[1]

The ore-bearing solutions are clearly differentiation products of normal igneous magmas, mainly of the pegmatitic facies, with abundant water and volatile constituents. Such solutions are not, however, derived from all magmas, and there is no general explanation of why some magmas are metalliferous and some are not. This is a fundamental fact of earth chemistry which has to be accepted without explanation. No doubt it is again a question of differentiation of earlier date and deeper seated character in regions inaccessible to observation.

The phenomena of vein-formation are most clearly shown in the case of acid magmas, especially granites. Basic magmas, as already explained, show much less pegmatitic differentiation, consequently vein-formation is also less common, the metals or sulphides, if present, tending to crystallize within the intrusion, as for example the chromite or metallic platinum in the ultrabasic rocks and sulphides of iron, copper and nickel in the gabbros and norites (see p. 123).

The effects of differentiation are seen not only in a concentration and localization of the metallic minerals (ores) but there is also a general succession of gangue minerals, also corresponding to temperature and physical conditions. Thus in the deepest and hottest zones are found tourmaline, topaz, quartz, felspar, and mica : above these come barytes, fluorspar and calcite, with often amorphous forms of silica, such as chalcedony, hornstone, etc.

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[1] Spurr, J. E., *Econ. Geol.*, vol. ii, 1907, pp. 781–795, and vol. vii, 1912, p. 489. *The Ore Magmas.* New York, 1923. Kemp, J. F., *Econ. Geol.*, vol. xvi, 1921, p. 474 and vol. xvii, 1922, p. 46. Davison, E. H., *Geol. Mag.*, vol. lviii, 1921, and *Handbook of Cornish Geology.* Penzance, 1925. Cronshaw, H. B., *Trans. Inst. Min. Met.*, vol. xxx, 1921, p. 408.

To take a concrete example, in the important mining district of West Cornwall around Camborne and Redruth the following zones of mineralization can be traced around the granite intrusions of Carn Menellis, Carn Brea and Carn Marth, beginning at the inside.

(*a*) Tin, tungsten and arsenic ores, with tourmaline and fluorspar.
(*b*) Copper ores, with quartz and fluorspar.
(*c*) Lead and zinc ores, with quartz and fluorspar.
(*d*) Iron ores with calcite.

These minerals are localized in lodes, lying in the granite and slate, but the zonary arrangement is clear both in the horizontal and vertical planes. (Instead of zones, it would be more correct to speak of shells.) The arrangement is obviously controlled by temperature, which is proportional to the distance from the granite: the boundaries of the zones being in fact curved, dome-like isothermal surfaces, which are now intersected by the denudation plane.

The same general succession, tin, tungsten, copper, zinc, lead, silver and iron seems to hold in many mining districts in all parts of the world. In Western America, where gold is abundant, the chief deposits come either between tin-tungsten and copper, or else along with silver above the lead zone. For some unknown reason the gold zones are missing in the British Isles. In the Western States and in other districts also antimony, bismuth and mercury zones follow on the highest given above, mercury ores being often deposited close to the present surface by hot springs and gas jets of visible volcanic nature.

All these metallic compounds in the order here given clearly form a differentiation sequence, being extracted from the granite in the form of volatile compounds or aqueous solutions at a high temperature and deposited along a falling temperature gradient in the order of their freezing points in the complex systems, which of course is not necessarily, or even probably, the order of the freezing points of the isolated minerals under laboratory conditions. The majority of the metals are actually deposited as sulphides, the chief exceptions being tin, tungsten and native gold. The last named often comes in the upper zone as tellurides, but in the lower zone it occurs in solid solution in copper and iron sulphides and arsenides (copper pyrites and mispickel).

The above is the sequence of ore-deposit from acid and intermediate magmas. In the basic and ultrabasic rocks the metals are different, as is also their manner of occurrence. This subject cannot, however, be pursued further here. For details reference should be made to some special treatise.

CHAPTER VI

MINERAL FORMATION IN IGNEOUS ROCKS

The Theory of Mineral Formation in Igneous Rocks. At this point it will be profitable to devote a little space to a more or less theoretical and generalized discussion of a small number of simple cases of crystallization of rock-forming minerals from silica melts. It must be understood that the whole subject is extremely complex, and the time has not yet arrived for a complete treatment of even a comparatively simple natural magma, but sufficient data of observation and experiment have been collected to allow of a discussion of certain simple cases, which may serve to show the lines to be followed in future work. Hitherto only a very few systems have been worked out in anything like completeness, and in particular our knowledge of the physical chemistry of acid magmas is less complete than that of some of the more basic types. This is due mostly to the apparent abundance in acid magmas of the so-called mineralizers, which as before shown also tend to accumulate in the later stages, whereas if present at all in the basic magmas, they appear to escape at an early period, or to take part in the formation of minerals of early crystallization. Consequently some basic magmas can be considered as reduced to fairly simple systems. It is chiefly with the minerals of basic rocks that we shall deal here.

As a simple example let us take a typical gabbro magma. A normal gabbro may be regarded as consisting of a basic plagioclase felspar with more lime than soda, and pyroxene, with or without olivine. The common accessories are ilmenite, apatite and pyrite: these are all very insoluble in silicate melts and crystallize early, so that for our present purpose they may be disregarded. The components of the system therefore are as follows: SiO_2, Al_2O_3, MgO, FeO, CaO, Na_2O. (Any Fe_2O_3 that may be present would come out early with an equivalent amount of FeO as magnetite. There is usually also a little potash, which enters into solid solution as the orthoclase molecule in plagioclase.)

Since in most common minerals FeO and MgO are isomorphous (vicarious) the actual number of components may be taken to be five. In most gabbros the bases (Mg, Fe)O and CaO are abundant, so that in many cases the ferromagnesian minerals crystallize before the felspar. In other instances, especially where alumina is high, felspar may come first, giving the ophitic structure. It must be considered therefore that these components group themselves into the following compounds :

$Na_2O.Al_2O_3.6SiO_2$ . . .	Albite	plagioclase
$CaO.Al_2O_3.2SiO_2$ . . .	Anorthite	
$CaO.(Mg,Fe)O.2SiO_2$ . . .	Pyroxene.	
$2(Mg,Fe)O.SiO_2$ . . .	Olivine.	

the relative proportions of the minerals being adjusted so that the whole of the material is used up.

We must now consider in a little more detail the physico-chemical and thermal relations of the systems represented by each of these minerals.

The Plagioclase Felspars. It has already been noted briefly in Chapter II that the plagioclase felspars form an admirable example of a system of two components showing complete miscibility in both the liquid and solid phases (Type I of Bakhuis Roozeboom). This system has been very completely investigated at the Carnegie Institute at Washington by Day and Allen and by Bowen.[1] Fig. 51, copied from Bowen's paper, shows the forms of the liquidus and solidus curves. Owing to the high viscosity of the melts richest in soda the data near this end are somewhat uncertain, crystallization being obtained only with difficulty.

Throughout this series true equilibrium can only be obtained with extremely slow cooling and zoned crystals are therefore very common in natural rocks, more especially in the hypabyssal and volcanic types. It is unnecessary to describe the characteristic twinning of the plagioclase felspars : it will suffice to note that as a rule the twin-lamellæ are narrower and more numerous in varieties richer in soda. Arbitrary names are applied to different varieties, but it must be insisted on strongly that in reality the plagioclases form a perfectly continuous series, the physical properties being in all cases simple linear functions of the chemical composition. The general formula of the group may be written $Ab_m An_n$. the coefficients m and n being now usually expressed as percentages :

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[1] Day and Allen, *Carnegie Institute Publication* No. 31. Bowen, *Amer. Journ. Sci.*, vol. xxxv, 1913, p. 577, and Alling, *Journ. Geol.*, vol. xxix, 1921, p. 194.

e.g. $Ab_{72}An_{28}$. Most plagioclases also contain a small percentage of the orthoclase molecule in solid solution. In all textbooks of petrology tables and diagrams will be found showing the variation of physical properties with the composition.

The alumina and soda having now been disposed of, there remain the constituents of the ferromagnesian minerals to be dealt with. These are MgO, FeO, CaO and SiO_2. For the sake of simplicity and convenience it is permissible to ignore the presence of FeO in an ideal case, and in reality this procedure is probably justified, since so far as is known the silicates of magnesia and iron, both metasilicates and orthosilicates, possess complete isomorphism and can form mixed crystals in all proportions : in the case of the other pair, however, MgO–CaO, this is certainly not true.

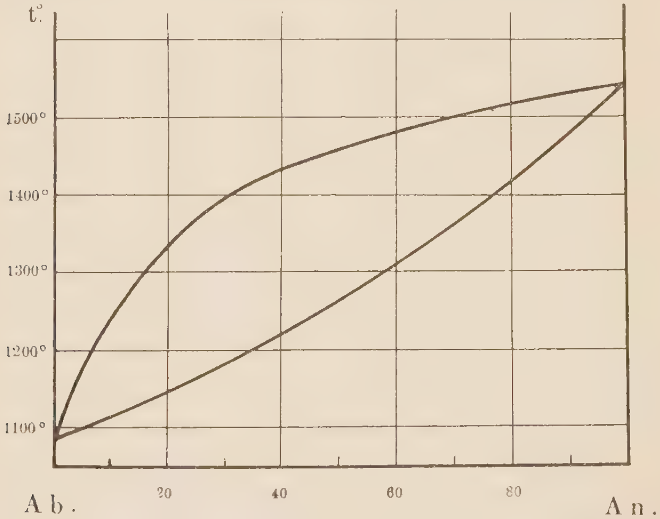

FIG. 51.—The liquidus and solidus curves for the albite-anorthite series. (From Bowen, *Amer. Jour. Sci.*, vol. xxv, 1913, p. 583.)

The System MgO–SiO_2. It is a curious fact that the thermal relations of the system MgO–SiO_2 are much simpler than those of the corresponding system CaO–SiO_2, in that there are not so many intermolecular compounds and polymorphic inversions : in fact magnesia and silica form only two compounds, $MgO.SiO_2$ and $2MgO.SiO_2$, corresponding to enstatite and forsterite in natural minerals. The first-named is capable of existing in three or four different modifications : the nature of these and their mineralogical characters will not be dealt with here, attention being confined to the behaviour of the form obtained in artificial melts, clinoenstatite, a mineral which curiously enough only occurs in meteorites. In practice it differs mainly from enstatite in having oblique extinction, and therefore belonging to the monoclinic system. The artificial orthosilicate on the other hand resembles natural forsterite in every essential respect and does not seem to undergo any enantiotropic or monotropic modifications.

These two compounds, as well as the end-products, periclase MgO and cristobalite SiO_2, can be obtained by fusing together their constituents in the proper proportions. The range of temperatures necessary for the whole system is very high, since the melting

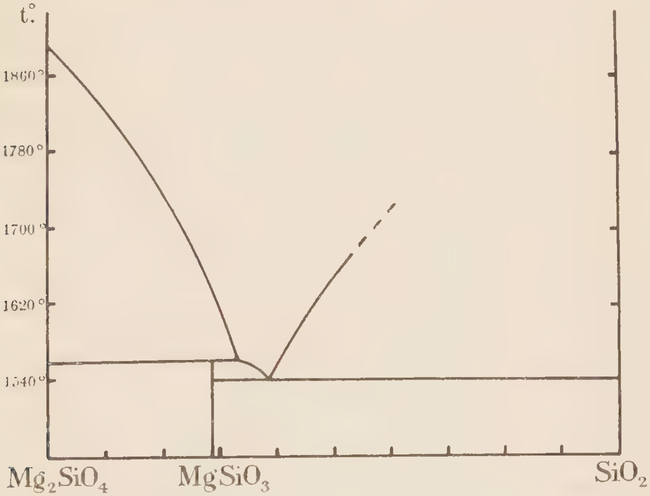

FIG. 52.—Thermal diagram for the system forsterite-silica, showing the incongruent melting of clinoenstatite to forsterite and liquid.

(From Bowen, *Jour. Geol.*, vol. xxx, 1922, p. 182.)

point of pure MgO has been determined by Kanolt as 2,800° approximately. Forsterite melts at 1,890° and cristobalite at 1,710°. Forsterite forms a eutectic with periclase at 1,850°, while the eutectic temperature for clinoenstatite and cristobalite is 1,543°, at 65 per cent. SiO_2 and 35 per cent. MgO.

We now come to a most important point, namely, that clinoenstatite has no true melting-point, but at 1,557° it begins to melt incongruently, being transformed into forsterite and liquid, thus:

$$2MgSiO_3 \rightleftharpoons Mg_2SiO_4 + SiO_2.$$

There is therefore no eutectic between clinoenstatite and forsterite, but a break occurs on the freezing-point curve, as shown in the figure. From this relation it follows that in the crystallization of a magnesian magma over a wide range of composition forsterite that first separates is later either partly or completely redissolved, reacting with the liquid to form a pyroxene. This is a necessary result of the equilibrium and it accounts quite readily for the very common presence in basic igneous rocks of a reaction-run (kelyphitic fringe or corona) of enstatite around olivine crystals. These have often been taken to imply some change of physical conditions during cooling, but this assumption is quite unnecessary.

The thermal relations of the binary system $MgO–SiO_2$ as above outlined are set forth in the diagram, Fig. 52, slightly modified from the one given by Bowen and Andersen, so as to incorporate a more recent determination of the melting point of cristobalite and with a small alteration in the neighbourhood of the transformation point of clinoenstatite.

As before mentioned all natural magmas contain ferrous oxide as well as magnesia, but it is unlikely that this causes any fundamental change in the general properties of the system, although it is extremely probable that most of the freezing-points are considerably lowered owing to the well-known fluxing properties of iron. The freezing point of the iron orthosilicate Fe_2SiO_4 is undoubtedly some hundreds of degrees lower than that of forsterite, while the freezing points of common olivines are believed in all cases to lie between these extremes; that is to say, Mg_2SiO_4 and Fe_2SiO_4 form a system of Type I, like the plagioclase felspars. However, the data for the construction of the ternary diagram $MgO–FeO–SiO_2$ do not yet appear to be available, and great difficulties, probably insuperable, are encountered in the investigation of melts containing FeO, owing to the ready oxidation of ferrous to ferric iron and corrosion of platinum apparatus.

The System $MgO–CaO–SiO_2$. It is unnecessary for our present purpose to give a full account of this very complicated ternary system. The chief point of importance is that $MgSiO_3$ and $CaSiO_3$ combine in simple molecular proportions to form a definite compound $CaMgSi_2O_6$ which is called diopside: its freezing point has been very exactly determined at 1,391°, and this may be taken as a fixed point in high-temperature thermometry and used for the calibration of apparatus. The end compound, $MgSiO_3$, occurs fairly commonly as enstatite, or with a certain proportion of FeO as bronzite and hypersthene, but pure $CaSiO_3$ is unknown in igneous rocks, being only found in metamorphosed limestones, as wollastonite.

The Relations of Augite and Plagioclase. Assuming now the existence of a magmatic melt which will eventually solidify as a mixture of pyroxene and felspar, that is, a normal gabbro magma, it remains to explain the laws governing the crystallization of such a solution. The first point is the choice of components: as just stated diopside is a definite compound and can be taken as one component, but since the felspars constitute a complete mix-crystal series they have to be treated as two components and the system becomes ternary, since diopside can be in true equilibrium with any member of the series. There is thus no true eutectic diopside-plagioclase, but a series of solutions all of which are in equilibrium with solid felspar of some composition, and the solid felspar must contain more of the higher-freezing component than the liquid does, in agreement with the principle set forth in the study of a binary system with complete solid solution. The ternary model thus becomes a combination of those representing a simple eutectiferous system and Type I of Roozeboom. This can be represented more or less satisfactorily in a plane diagram as shown in Fig. 53; the two surfaces *D Di F* and *Ab D F An* represent the liquidus surfaces, but in the lower half of the figure there should also be a solidus surface, which cannot be shown. However, the short straight tie lines inclining back to the right give the composition of the solid felspar in equilibrium with the liquids represented by the corresponding points on the

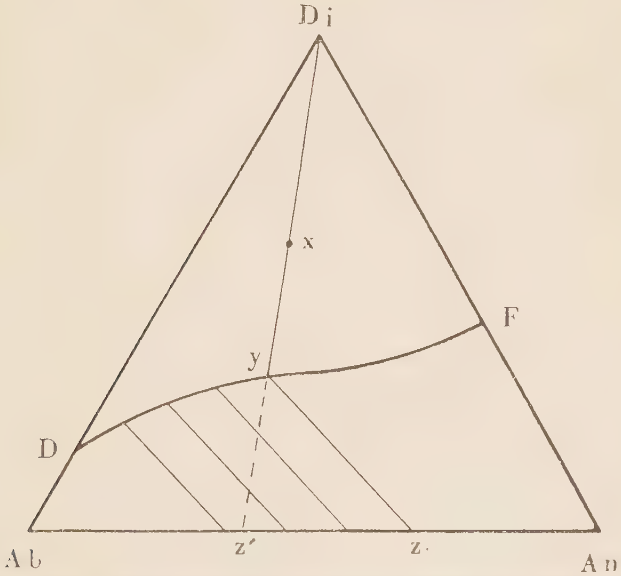

FIG. 53.—The course of crystallization of the system diopside-plagioclase. (From Bowen, *Jour. Geol.*, vol. xxx, 1922, p. 180.)

line D F. This line is sometimes called the "*eutectic boundary*" and is in effect the bottom of a valley running across the liquidus surface, and inclined downwards to the left. The most important point to be remembered in this system is that the pyroxene is constant in composition, being always diopside, while the felspar varies as crystallization proceeds, but if the full equilibrium is established it should in the end be of uniform composition, just as in the simple felspar system without pyroxene.

The course of crystallization of a melt represented by the point x is obtained as follows: from the point Di draw a straight line through x to cut the eutectic boundary line in y. From x to y diopside separates, but at y the solution is in equilibrium with a felspar of the composition given by the tie-line yz. This begins to separate, but the principle of continuous reaction then comes into play as before (see p. 32). The final result will be a mixture of diopside and a felspar of the composition given by the point z', corresponding to the average composition of the original melt. The possibility of delayed equilibrium and zoned felspars is of course not excluded.

Olivine. If the original melt contained more magnesia than was required to combine with the lime to form diopside, there will take place formation of enstatite or olivine, or both, according to the ratio of magnesia to silica. According to the latest work on the subject, owing to the incongruent melting of clinoenstatite, the material of the rhombic pyroxene should in all probability separate first as olivine, being later converted to enstatite by reaction with the liquid. As before mentioned some olivines in basic rocks do show a skin of rhombic pyroxene (kelyphitic fringe) and it is probable that the very rounded form of grains of olivine in certain rocks with the so-called pœcilitic structure is due to the same reaction, the limit of the inversion being fixed by the increasing viscosity of the residual liquid.

In certain rocks of very basic composition but with a fair amount of alumina pyroxene is entirely absent and the whole magma crystallizes as felspar and olivine. The rock of the Isle of Rum, described by Harker as allivalite, is a good example.[1] The typical rock, near the summit of Allival, consists of about equal proportions of anorthite and olivine, with a very little pyroxene and magnetite. The ratio MgO : FeO is about 3 : 1 by weight, therefore, the olivine contains a large proportion of the forsterite molecule. The figures are[2] Fe_2O_3, 1·20; FeO, 6·33; MgO, 20·38 per cent.

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[1] Harker, *The Geology of the Small Isles*, Mem. Geol. Survey, Scotland, 1908, p. 79.

[2] *Op. cit.*, Analysis III, p. 80.

Since there is a little magnetite a proportion of the FeO equivalent to the Fe_2O_3 has to be subtracted and the calculation becomes

		Magnetite.	Olivine.	Ratio.
SiO_2	17·70 ÷ 60 = ·2950	—	·2950	3·67
Fe_2O_3	1·20 ÷ 170 = ·0075	·0075	—	—
FeO	6·33 ÷ 72 = ·0879	·0075	·0804	1·00
MgO	20·38 ÷ 40 = ·5095	—	·5095	6·34
		·0150	·8849	

thus giving a ratio $FeSiO_4 : Mg_2SiO_4 = 1{\cdot}50 : 9{\cdot}51$. Hence it is seen that the olivine contains about six times as much of the forsterite as of the fayalite molecule.

Other members of this group contain varying ratios of olivine and anorthite and in these an interesting phenomenon is seen, as described by Harker. It is found that the order of separation of the two minerals depends on their relative concentration; the one that is in excess always crystallizes first, thus showing that the system in its final stages approximates at any rate to the simple eutectiferous type, where the component in excess of the eutectic ratio separates first, whatever may be the freezing points of the pure components. In the closely related eucrites, however, which carry a fair amount of pyroxene, the olivine always crystallizes first, showing the influence of the common magnesium ion, in accordance with Nernst's Law.

The Norites. These form a well-known and fairly well-defined rock-group, differing from the gabbros mainly or entirely in the presence of a considerable amount of rhombic pyroxene, enstatite or hypersthene. From the chemical standpoint this means that the magma contains only about enough lime to saturate the alumina to form felspar, while the magnesia and iron then combine as a rhombic pyroxene, with or without olivine. The constitution of the norites has been very carefully investigated by Vogt, in consequence of the curious and still unexplained fact that the sulphide deposits found in connection with these rocks commonly carry workable percentages of nickel with or without copper, whereas the gabbros with dominant monoclinic pyroxenes are usually associated with sulphides of iron and copper only. This fact is strikingly illustrated by the nickel deposits of Norway and of Sudbury, Ontario; the last-named is the most important nickel-deposit of the world. Vogt has come to the conclusion that many norite magmas must originally have been very close to a eutectic (or eutectic boundary line) in composition: this is shown partly by the fact that both felspar and pyroxene have crystallized at approximately the same time.

The Intermediate Alkaline Rocks. The distinguishing characteristic of this group is the presence of an unusually high percentage of alkalis, potash or soda or both. Many of them carry an even higher percentage of these oxides than the granites, whereas in the calc-alkaline suite the proportion of soda (and potash) rises steadily from the ultrabasic to the most acid members. Consequently in the intermediate members of the alkaline suite there is often more alkali than can be saturated by silica to form orthoclase or albite, which may be regarded as the standard minerals, which will be formed if possible. The result is, in such a case, the crystallization from the magma of some member of the felspathoid group, usually with, but sometimes without, felspar. The equilibrium relations can be simply expressed by the two following equations :

$$\underset{\text{Nepheline.}}{Na_2O.Al_2O_3.2SiO_2} + 4SiO_2 \rightleftharpoons \underset{\text{Albite.}}{Na_2O.Al_2O_3.6SiO_2}$$

$$\underset{\text{Leucite.}}{K_2O.Al_2O_3.4SiO_2} + 2SiO_2 \rightleftharpoons \underset{\text{Orthoclase.}}{K_2O.Al_2O_3.6SiO_2}$$

the equilibrium under conditions of cooling and crystallization always lies on the right-hand side : the practical effect is that from an arbitrary mixture of the components of these silicates either a felspathoid and a felspar, a felspar alone, or a felspar and quartz will separate, according to whether the ratio of silica to alkali is less than equal to, or greater than 6 : 1 (alumina being supposed constant with a ratio to the alkali of 1 : 1). But it is

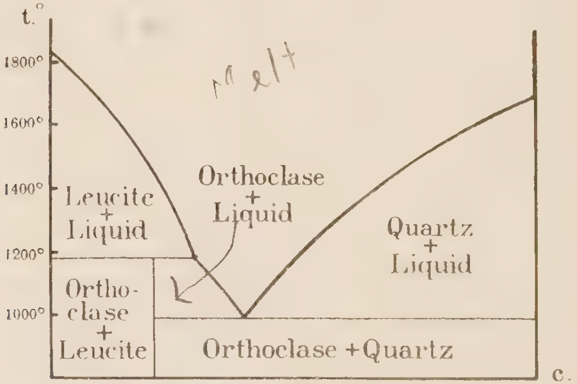

FIG. 54.—The system orthoclase-leucite-silica, showing incongruent melting of orthoclase to leucite and liquid (after Bowen).

not possible for a mixture of a felspathoid and quartz to crystallize out. It has lately been shown by Bowen that in the second of these equations the equilibrium shifts to the left on heating to a high temperature, or in other words that orthoclase has no true melting point, but melts incongruently to leucite and a liquid. A similar effect has not been observed in the case of albite.

When silica is in excess of the above named ratio, quartz is formed and the rock is called a quartz-syenite or a granite : with felspar alone it is a normal syenite, while the more basic varieties are nepheline-syenite or leucite-syenite, the last-named being a very rare type. Sodalite-syenites also exist in considerable quantity, but the sodalite is believed to be an alteration product of nepheline, probably brought about by solutions containing chlorine (perhaps a type of pneumatolysis). In all these rocks the felspar very commonly shows some type of perthitic structure.

Basic Alkaline Rocks. There are also known numerous examples, though not in great total amount, of rock-types of distinctly low silica percentage, comparable to gabbros in this respect, but characterized by the presence of more or less felspathoid minerals or highly alkaline felspars. In these the magnesia and iron are high, some containing olivine, while the lime of the calc-alkaline rocks is largely replaced by soda or potash : there must also be a fairly high alumina ratio. Thus are formed various types of nepheline-gabbro, leucite-gabbro, and peculiar rocks with nepheline or leucite, but no felspar. In hypabyssal types analcime is common (teschenites). The laws governing the crystallization of such magmas should be obvious from what has already been said and the subject need not be pursued further here. It may be noted that these highly alkaline basic types, when intrusive, are usually small differentiates from larger masses : basic alkaline lavas occur in considerable quantity, as at Vesuvius and many of the extinct Italian volcanoes, while teschenite sills of fairly large size are pretty common. In some volcanic rocks that really belong here the alkaline character is only revealed on chemical analysis and not by microscopic examination, since the alkalies tend to concentrate in a residual glass, if such is present.

Crystallization of Granitic Magmas. Under this category, in accordance with the ordinary nomenclature of petrology, are comprised all rocks in which silica is present in a proportion so high that it more than suffices to saturate all the bases as silicates, the excess then crystallizing as quartz. As a matter of empirical observation in such types it is found that as a rule the alkalies and alumina are also high, whereas lime, magnesia and iron are relatively low. Hence alkali felspars are the dominant and characteristic minerals, commonly with mica and often hornblende. The most acid types often carry muscovite, with or without biotite: those with a rather lower silica percentage and more iron and magnesia contain biotite or hornblende or both: while augite and hypersthene granites are rare. In certain types with an unusually large amount of soda, this oxide enters into the constitution of special varieties of amphibole or pyroxene, such as riebeckite or aegirine, which are likewise found in the syenites: soda-granites only differ from soda-syenites in the presence of quartz and there is a complete transition through quartz-syenites, such as the Norwegian nordmarkite.

It appears that in magmas of a high degree of acidity there is generally present a considerable proportion of constituents of a peculiar character, which tend to concentrate in the last residues of the crystallizing solution, at any rate in the case of the deep-seated plutonic intrusions. From the hypabyssal, and still more from the volcanic types, they commonly escape before crystallization approaches completion, and these types are therefore on the whole simpler in their general relations. These constituents of the magma comprise not only water and certain volatile elements of low atomic weight, such as boron and fluorine, but also many of the heavy metals that give rise to ore deposits. These will not here be taken into account, being dealt with elsewhere (see p. 200). Attention will be confined mainly to the laws governing the formation of the "essential" minerals of the granites; quartz, the felspars, the micas and hornblende, the less common types being ignored. The so-called "accessory minerals" are also dealt with in a separate section (p. 130).

For our present purpose then a normal granite magma is to be regarded as a system of the following components: SiO_2, Al_2O_3, K_2O, Na_2O, CaO, MgO, FeO. This system as it stands is evidently too complex to be reduced to the exact quantitative treatment of the phase rule, but certain simplifications can be made. In the first place, the magnesia and ferrous iron are the least soluble in a silicate melt and separate first: if abundant relatively to the alkalies as hornblende, if in lower proportion they may enter into a mica molecule, biotite or phlogopite, or their soda analogues. Further, any proportion of lime that may be present commonly combines as the anorthite molecule and enters into solid solution with the albite molecule as some form of plagioclase; very often oligoclase. However, in many granites the ratio CaO : Na_2O is so low that the anorthite can be swallowed up in alkali felspar very near to albite. We are thus left with a final solution of SiO_2, Al_2O_3, K_2O and Na_2O, together with a certain amount of water.

From such a mixture the minerals that can separate are felspars and micas, with or without quartz. For the sake of simplicity all the alkalis may be regarded as potash : then the theoretical possible solid phases will be :

$$\begin{aligned} K_2O.Al_2O_3.6SiO_2 &= \text{orthoclase} \\ K_2O.Al_2O_3.2SiO_2 &= \text{muscovite} \\ SiO_2 &= \text{quartz} \end{aligned}$$

As a matter of fact in muscovite some of the potash is always replaced by water, the composition often approximating to the ratio $2H_2O.K_2O.3Al_2O_3.6SiO_2$, but the ratio of $K_2O : H_2O$ is variable within fairly wide limits. In this case it is evident that the final content of muscovite will be controlled partly by the presence of water, but necessarily to a large extent by the alumina-silica ratio. From certain facts set forth in the chapter on weathering it is clear that the orthoclase-muscovite-water equilibrium is variable and reversible, as may be set forth in the following somewhat loosely constructed equation.

$$\underset{\text{Orthoclase.}}{xK_2O.Al_2O_3.6SiO_2} + yH_2O = \underset{\text{Muscovite.}}{(H,K)_2O.Al_2O_3.2SiO_2} + 4SiO_2$$

This is the expression of the process known as sericitization.

However, in the granitic magma the practical result is that the excess of alumina, if present, is adjusted between felspar and mica, and the mica usually crystallizes before the felspar, leaving a final residue which may crystallize as a mixture of orthoclase (or microcline) and quartz.

Everything said in the foregoing paragraph also holds good, *mutato nomine*, if soda is substituted for potash, the minerals formed being paragonite (soda-muscovite) and albite ; the only real difference is that albite can enter freely into solid solution with a lime-felspar molecule, which orthoclase can only do to a very small extent.

The Crystallization of the Alkali Felspars. We must now consider somewhat in detail the properties of a binary system in which the components are orthoclase and albite, which can be conveniently abbreviated as Or and Ab. In spite of great practical difficulties in experimental work, which need not be enumerated here, this system has been carefully investigated, and is believed to afford an example of solid solution with limited miscibility of the solid phases. The data yet available are scarcely sufficient for the accurate construction of the full thermal diagram. It is of course an example of Roozeboom's Type V (see Fig. 17).

As before explained on general grounds it is impossible for a pure compound to separate from a mixed melt: all solid phases must necessarily be solid solutions while in equilibrium with the liquid phase, and even the final eutectic is a mechanical mixture of two solid solutions, whose composition is given by the points *D F* of the diagram. Another consideration of great importance is that in such a system the mutual solubility of the components of the solid solution also changes with fall of temperature, so that it is possible for conspicuous changes of structure to take place in the solid crystals even at temperatures far below the freezing-points. This phenomenon is very well known in metallic alloys, and is of first-class importance in the heat-treatment of metals. It undoubtedly explains also the peculiarities of structure in alkali-felspars commonly known as perthitic structure. In some such felspars it is quite easy under the microscope with crossed nicols to distinguish lamellæ or lenticular inclusions of twinned plagioclase embedded in orthoclase; in other cases merely a general cloudy appearance is produced, which is often accentuated by slightly differing degrees of decomposition in the two constituents. In other instances, however, felspars showing on analysis both potash and soda appear perfectly clear and homogeneous. These are often called soda-orthoclase, or anorthoclase.

From this diagram, however, it is clear that there must be *two* possible solid solutions of orthoclase and albite, of differing composition: therefore two distinct things are included under the name of perthite. The author is not aware that so far any criterion has been found for discriminating between them.

The Influence of Eutectic Composition on Rock-structures. When in the final stages of crystallization a silicate magma has attained eutectic composition after separation of the components in excess of the eutectic ratio, two (or more) solids are then in equilibrium with the liquid. This in effect means that two (or more) minerals are crystallizing at the same time. It might be expected, therefore, on general grounds that they would show distinctive mutual space-relations.

It is well known that in very many rocks quartz and felspar occur in what is known as "graphic intergrowth," the name being derived from a supposed resemblance to Hebrew letters. This occurs both on a large scale in certain pegmatites and microscopically in many rocks with free quartz (micropegmatite). Since pegmatites are obviously formed by crystallization of magmatic residues the occurrence of this structure is highly suggestive, and Teall[1] long ago directed attention to the fact. The subject has also been studied in much detail by Brögger and by Vogt,[1] in continuation of Teall's work. Numerous bulk-analyses of large samples of graphic granite were made. Without entering into details it may be said that the evidence shows that the eutectic quartz-orthoclase lies at about 74 per cent. orthoclase to 26 per cent. quartz, by weight. Vogt extends this generalization to the fine intergrowths of quartz and felspar seen in granophyric, micro-spherulitic and microfelsitic rocks, and also to the glassy base of many hypabyssal and volcanic rocks, in all of which the ratio of silica to felspar-molecule as shown by analysis is nearly constant.

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[1] Teall, *British Petrography*. London, 1888.

Later the view was put forward, especially by certain American writers, that the occurrence of graphic intergrowth is a by no means necessary result of eutectic or nearly eutectic composition, but that many varieties of rocks showing the ordinary hypidiomorphic or granular structure are in point of fact eutectics, or nearly so. Something of the sort is probably indicated by the curiously sharp limitations of the possible range of composition, especially in the acid rocks. True granites rarely show more than about 76 per cent. SiO_2 in the most highly alkaline varieties, while with increase of lime the maximum silica percentage in known rock types seems to fall pretty steadily. Rocks with much oligoclase, for example, seldom seem to show more than 68 per cent SiO_2. These facts certainly indicate that the addition of lime decreases the proportion of silica in the quartz-felspar eutectic. The excess of silica in all cases is doubtless removed in watery solution to form quartz veins.

Eutectics and Crystallization of Magmas. From a detailed consideration of many facts of observation and points of theory similar to those just mentioned, it was realized by petrologists many years ago that the laws of solution and in particular the study of eutectiferous systems throw much light on problems of petrogenesis, and for a long time the theory of eutectics was regarded as of primary importance. It certainly led to many very valuable results. But it has also been realized that even in very simple systems, involving only two or a very small number of components, other relations may hold, excluding the formation of a eutectic. Such for example is the principle of continuous reaction in the case of complete solid solution: also certain instances of incongruent melting complicate matters a good deal. It is therefore clear that the consideration of the eutectic principle cannot be extended to all cases, or perhaps even to the majority of cases. Nevertheless it certainly does hold in a general way in the crystallization of some simple magmas and also, which is perhaps of the greatest significance, in the solidification of magmatic residues, such as give rise to the many varieties of pegmatite dykes and veins, in which are concentrated the less abundant constituents of the igneous rocks, including therein a good many examples of ore-deposits.

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[1] Brögger, *Zeits. für Krist.*, vol. xvi, 1890, pp. 148–159. Vogt, *Die Silikatschmelzlösungen*, Part II, 1904, pp. 117–125.

Further, it has been suggested many times that the eutectic principle is of fundamental importance in the phenomena of magmatic differentiation. In this respect the remarks in the foregoing paragraph apply with equal force. The whole subject is, however, still in a somewhat speculative and transitional stage : it is too complicated to be dealt with here in detail. Those specially interested in the subject may be referred to an excellent summary by Bowen in the publication quoted in the footnote.[1]

The Accessory Minerals. So far attention has been confined mainly to the laws governing the crystallization of the abundant and characteristic minerals of the different rock-groups ; ferromagnesian minerals, felspars and felspathoids, and quartz of the ordinary classification. But it is well known that all or nearly all igneous rocks also carry small, and often very small, amounts of other minerals, which are of interest, although they have no bearing on classification : sometimes, however, either in their primary state or when concentrated in sediments they are of commercial importance, e.g. platinum, monazite, tinstone, gold.

It is of course difficult, if not impossible, to draw up an exact definition of an accessory mineral, inasmuch as a mineral which is accessory in one rock may be essential in another, but the term in a general sense is fairly well understood, and need not be interpreted too strictly. In a broad way it is true that the accessory minerals contain the less abundant chemical constituents, but not invariably or necessarily, since analyses of isolated minerals have often shown such in the more abundant species, e.g. small amounts of heavy metals or rare earths in ferromagnesian minerals, while micas often carry lithium, fluorine, etc. In many of these instances, however, there is always a possibility of solid inclusions in the material analysed, for example, zircons in mica, a very common occurrence.

At present our knowledge of the accessory minerals is less complete than could be wished, since their determination depends chiefly on the microscopic examination of thin slices, where the chances of missing a rare mineral are great. This can, however, be remedied by crushing the rocks and examining the powder by concentration, magnetic separation and heavy liquids.[2] In this way, unexpected results may sometimes be attained. This treatment is in fact an imitation of the methods of nature in the concentration of black sands, gem gravels, and gold-bearing alluvials.

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[1] Bowen, " The Reaction Principle in Petrogenesis," *Journ. Geol.*, vol. xxx, 1922, pp. 177–198.

[2] Rastall and Wilcockson, " The Accessory Minerals of the Granitic Rocks of the Lake District," *Quart. Journ. Geol. Soc.*, vol. lxxi, 1915, pp. 592–622.

As a general rule it is found that the accessory minerals crystallize at an early stage in the consolidation of a magma. It is usually stated that this is because their freezing points are very high, and in many instances this is undoubtedly true. However, this relation can be expressed in a more satisfactory and more general form by the statement that the accessory minerals are those possessing a very small degree of solubility in a silicate magma, from which they consequently separate at an early stage. Hence they often show very perfectly developed crystal forms, and are often clearly enclosed in larger crystals of the later minerals.

No attempt will be made here to give a complete list of the accessory minerals known to occur in igneous rocks: but a few well-known ones will be selected as characteristic of the different groups, acid, intermediate and basic. In the granites are found a large assemblage, of which the most widely-distributed are magnetite, apatite, sphene and zircon. Others of less common occurrence are epidote, allanite, monazite, garnet, beryl and various sulphides, especially pyrite. The occurrence of tourmaline and fluorite is of a special character, since they are often obviously secondary, a result of the class of phenomena commonly, though perhaps not quite satisfactorily, called pneumatolysis. Some of those here mentioned are specially characteristic of pegmatites, e.g. garnet and beryl, and no satisfactory line can be drawn between these and the minerals of the true mineral veins.

In the syenites are found most of those common in granites, with, in addition, corundum, and in many of the syenitic pegmatites a great concentration of rare-earth minerals, which need not be enumerated. In the basic rocks the differences are rather more marked. Here instead of magnetite we often find ilmenite, while chromite and other spinel minerals are characteristic, sometimes accompanied by metallic platinum and other metals of that group. Again, sulphides are more abundant, often including nickel sulphides, nearly always accompanied by a smaller proportion of cobalt. In some gabbros apatite is concentrated in considerable quantity, but differing from the apatite of the granites in the presence of chlorine instead of fluorine. In the pegmatitic modifications of the basic rocks the most characteristic elements are usually titanium, phosphorus and chlorine, while in the normal rocks there is often a good deal of vanadium, though it is not clear in what minerals this is combined. A not uncommon result of the presence of chlorine in the residual solutions of gabbros is the conversion of the plagioclase felspars into scapolite.

In general the accessory minerals of the hypabyssal and volcanic rocks are the same as those of the corresponding plutonic types, though often less conspicuous in slides owing to the difference in structure and in some instances the large amount of interstitial dark-coloured glass, which tends to mask small crystals. Very often the dark colour of this glass is itself found to be due to minute grains of some iron oxide, magnetite or ilmenite, scattered through it.

It is sometimes observed even in granites that magnetite occurs in two generations, one early and idiomorphic, the other late and interstitial. The early-formed crystals evidently represent the excess of magnetite insoluble in the melt at that early stage, while the later magnetite is the part of the original content that remained in solution in the magma to a lower temperature, possibly remaining dissolved right down to the solidification of a eutectic residue. In some cases, however, it is clear that magnetite has separated at a late stage as a result of reactions between silicate minerals, according to Bowen's principle of discontinuous reactions.[1]

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[1] See reference cited on p. 130.

CHAPTER VII

METAMORPHISM

Definitions. In the majority of writings on metamorphism, even up to the most recent times, the assumption is made either explicitly or tacitly, that the subject can be divided into two definite and distinct categories, depending on whether the observed effects are due to increase of temperature or increase of pressure, the categories being usually named thermal and dynamic metamorphism respectively. But this is not at all a satisfactory method of regarding the matter, and is in need of revision. It is quite true that there are simple cases where the phenomena are mainly due to rise of temperature and other cases where they are mainly due to increase of pressure, but these are in reality extreme instances: nearly always it is clear that both factors have been at work jointly, and both must be taken into account in any explanation of the results on any but the most empirical lines. The phenomena of metamorphism and the nature and extent of the changes brought about in rocks, are strictly functions of at least two independent variables, and neglect of this simple conception has led to the failure of more than one attempt at drawing up a classification of the resulting rock-types. This theoretical basis of the treatment of metamorphism is discussed very clearly by Harker in a Presidential Address to the Geological Society of London in 1918.[1] In this address special attention is paid to the important distinction that must be drawn between pressure that is equal and uniform in all directions ("hydrostatic" pressure), and shearing stress. As an example of the significance of this distinction attention may be drawn to the different effect of these two types of pressure on the melting-points of minerals. When the volume of the liquid form is greater than that of the solid form, hydrostatic pressure *raises* the melting-point, but differential pressure in the form of a shearing stress invariably *lowers* the melting-point, and that in a much greater degree. This produces important effects in a two-phase system, consisting of crystals with interstitial liquid.

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[1] *Proc. Geol. Soc.*, Session 1917–18, pp. lxiii–lxxx.

Another point of first-rate importance is that the same law applies in a general way to solution. It is obvious that in the usual case, where solution is accompanied by a decrease in the total volume, solubility will be increased by pressure, and this fact therefore favours flow and rearrangement in rocks under stress. The direction of least pressure is at right angles to the line of application of the force, and there will therefore be a tendency to solution of crystals in one direction, with recrystallization in the direction at right angles to it, thus leading to the formation of long crystals lying at right angles to the pressure, and in general to the production of leafy, bladed and prismatic forms, with, as a consequence, a foliated structure in the reconstituted rocks. Since it is very difficult to conceive of intrusion of igneous rocks unaccompanied by pressure, it is only natural to find that in most cases of so-called thermal or contact metamorphism there is developed, at any rate near the intrusion, a more or less definitely developed foliation of the altered rocks. In some instances, however, it is difficult to disentangle foliation produced in this way from the appearance of banding resulting from a primary stratification of sediments.

A further source of difficulty has arisen from a confusion between foliation of a secondary or induced character due to recrystallization under pressure in rocks of any class and primary foliation which is in point of fact a flow structure in igneous rocks. At one time it was generally believed, even by geologists of the greatest eminence, that a banded structure in crystalline rocks necessarily implied that these were once sediments, this doctrine sometimes being pushed to extreme lengths, but now it is generally recognized that nearly all intrusives show more or less banding due to flow of heterogeneous magmatic material, and where, as is often the case, intrusion has accompanied earth-pressures, this effect is often very strongly marked; particularly so where partly differentiated magmas have become partly re-mixed during intrusion in a pasty condition.

It is evident, therefore, that logically no hard and fast line can actually be drawn between the different classes of metamorphism: nevertheless, in order to render the subject in any degree intelligible it is necessary to make some form of artificial classification. There undoubtedly are cases where either heat or pressure has been the *dominant* factor, although in no case can the effect of the other agent be wholly excluded.

The precise name to be applied to each of these classes is a matter of no importance whatever: for convenience they will here be called *thermal* and *dynamic* respectively, since these words do at any rate imply the nature of the chief physical agent at work in each case and make no assumptions as to underlying causes.

The Time-factor in Metamorphism. From comprehensive studies of thermal metamorphism in many parts of the world it seems to be pretty clearly established that the extent of alteration produced is not solely a function of temperature and pressure, but that the duration of the processes has also to be taken into account. It appears that a moderate degree of temperature continued for a long time may produce more striking effects than a very high temperature applied for a short time only. This is connected with the low conductivity of rocks and the slow rate of diffusion of solutions. *Mutatis mutandis*, similar considerations apply to pressure: very high pressures acting for a short time may produce mainly shattering effects, mylonitization, etc., while a long-continued pressure will give rise to new minerals specially adapted by structure and high density to the conditions that prevail. To express the matter in a slightly different way, we may say that attainment of physico-chemical equilibrium is a very slow process in metamorphic as well as in igneous rocks, and in many cases it is in reality never attained at all.

Composition of Normal Sediments. As a preliminary to the study of the metamorphosed sediments it is essential to discuss very briefly the composition of the unaltered rocks. For this purpose the sediments can be separated into three broad groups, *arenaceous*, *argillaceous* and *calcareous*: of these groups sandstone, clay and limestone can be taken as typical examples, but of course every possible gradation exists between them. The list of chemical compounds present in the sediments is essentially the same as in the igneous rocks, though the proportions naturally differ widely. As the characteristic constituents of the three groups just mentioned, we can take silica, aluminium silicate and calcium carbonate. Sandstones and limestones are in some cases very nearly pure SiO_2 and $CaCO_3$ respectively, but the argillaceous rocks are more complex and are rarely free from notable amounts of magnesia, iron oxides, lime and alkalies. It is clear, however, that if we take SiO_2, Al_2SiO_5 and $CaCO_3$ as the components, the composition of sediments can be represented on a triangular diagram: the very important group rich in magnesium carbonate requires, however, special consideration. Some of the most interesting examples of thermal metamorphism are afforded by the argillaceous rocks with a notable though varying percentage of magnesia, and these have been studied with some degree of completeness.

Owing to considerations of space only a few typical and simple cases can here be considered.

Thermal Metamorphism of Siliceous Rocks. As is explained later in Chapter XI, the thermal relations and stability fields of the different forms of silica are well known and this to a high degree of accuracy. The study of the behaviour of mainly siliceous rocks in metamorphism is much simplified by the fact that owing to the prevalence in most cases of fairly high pressures the only stable form is that of the highest density, namely quartz: tridymite and cristobalite have never been observed in metamorphic rocks. All forms of silica, then, whether quartz, chalcedony, opal or the rather vague and indeterminate varieties found in organic (fossil) structures, undergo more or less complete recrystallization as quartz, the degree of reconstruction depending on the temperature and the rate of cooling. Under normal conditions, in the vast majority of cases the result is the production of a rock that can be referred to the general category of quartzites. A considerable variety of structures can be recognized but the differences are mainly in the degree of recrystallization. In the simplest case of a rock consisting of sand grains with a siliceous cement the distinction between grains and cement is often obliterated, the cement, if granular, being more or less completely reconstituted, in such a way that the molecules of the original cement orientate themselves in continuity with the crystalline structure of the larger grains, thus producing a mosaic of solid quartz. If, as sometimes happens, the cement is chalcedonic or opaline it will be converted to quartz, which behaves in a similar way. Sometimes the outlines of the original grains can still be distinguished, but if the alteration is very profound the whole rock may become a solid mass of interlocking quartz crystals often showing peculiar crenulated outlines. In such quartzites also, pressure often sets up differential strains and disturbs the optical properties of the crystals, so that extinction in polarized light becomes very confused (strain shadows). This effect is however more marked in purely dynamic metamorphism. There is one other possible case, which though rare, has been actually met with, namely, fusion of the silica and solidification as glass. An instance on a small scale in the island of Soay is described by Clough and Harker.[1] Here a grit belonging to the Torridonian series has been invaded by thin dolerite sills and the grit has been in great part vitrified by the sills, which must have been at a very high temperature. The grit contained a good deal of felspar and some iron oxide, which probably acted as a flux and lowered the fusion point of the quartz, so that this can scarcely be regarded as an instance of the vitrification of pure quartz. The whole of the felspar and iron oxides have gone into the glass as well as much of the quartz, while relics of quartz grains are enclosed in it.

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[1] Harker, *The Tertiary Igneous Rocks of Skye*, Mem. Geol. Survey, 1904, p. 245.

Argillaceous Rocks. We will first consider the physical chemistry of an ideally simplified case, namely that of a pure clay, which may be taken to consist of silica and alumina only, together with water in varying proportions. It may be mentioned in passing that this ideal case is very nearly realized in some fire-clays and pipe-clays. This subject is referred to again in the chapter dealing with refractories.

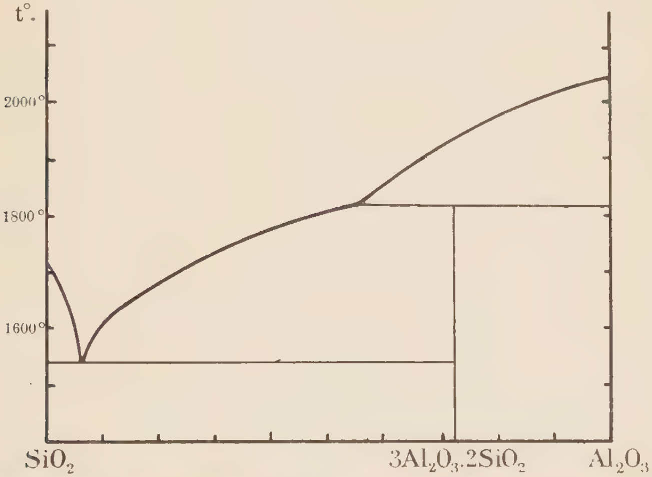

FIG. 55.—Equilibrium diagram of the system Al_2O_3–SiO_2, with incongruent melting of mullite.

(Bowen and Greig, *Jour. Amer. Ceramic Soc.*, vol. vii, 1924, p. 238.)

Although the water in such clays when undergoing metamorphism probably takes some part in the reactions that occur, for the present it can be safely ignored, since it does not appear in the final minerals produced, and the system can be regarded as containing SiO_2 and Al_2O_3 alone, being therefore a binary system, and lending itself well to elementary treatment. Until a very few years ago it was believed that these two components formed only one compound, Al_2SiO_5, but as a result of recent research it is now thought to be not quite so simple as this. Under natural conditions this compound is in fact usually formed, though not always, but under laboratory conditions the compound formed seems to be always

$3Al_2O_3.2SiO_2$: this has also been lately found in natural rocks in the island of Mull, and is therefore called *mullite*. The issue is further complicated by the fact that natural Al_2SiO_5 crystallizes in three distinct and very well-defined forms, as andalusite, kyanite and sillimanite, all of which are commonly found in metamorphic rocks. Their mutual relations are far from being completely known; it is clear that andalusite is the usual low-temperature form, and Vernadsky has shown that kyanite inverts to sillimanite at about 1,380° C. under atmospheric pressure.[1] Since kyanite has the highest density of the three it must be the stable form under high pressure, and it is very common in dynamic metamorphism, but the relations of andalusite to kyanite are not known. Kyanite is certainly a typical stress mineral.

In this system the actual melting points concerned are very high, those of Al_2O_3 and Al_2SiO_5 being certainly never reached in nature, while, as explained later, the thermal behaviour of mullite is peculiar. Since this system is of great technical importance in connection with refractories, its detailed consideration will be deferred for the present, and attention will be confined to the phenomena observed in the field where reasonably pure clay-rocks, such as shales or slates, have been thermally metamorphosed by an intrusion. It is, however, difficult to find any case which is not complicated by the presence of magnesia, iron and alkalies, which give rise to the formation of cordierite, staurolite, micas or even felspars. However, by combining a large number of observations from different areas it is clear that the first mineral to form when clay-rocks are heated is andalusite, often in the special form called chiastolite, a variety marked by inclusions of carbon arranged in the form of a cross. Such crystals may reach a very large size, several centimetres long, but very often the texture is finely granular, forming the rock-type known as andalusite-hornfels. When the temperature passes a certain limit the andalusite undergoes an inversion, and it seems to depend on the pressure whether it forms kyanite or sillimanite. Probably, beyond a certain temperature-limit, sillimanite must be formed, whatever the pressure, but this is a speculative subject. At any rate in a well-known case in the south-eastern Highlands, described by Barrow, kyanite gives place to sillimanite in the zone of highest grade metamorphism. Here the temperature-factor seems to be dominant over stress.

Of much greater practical importance are the more complex cases alluded to above, where other components are present, as in the great majority of argillaceous sediments. This subject has given rise to a voluminous literature of late years, and is very difficult to treat in an elementary fashion. Special reference must here be made to the writings of V. M. Goldschmidt on the Kristiania region and of C. E. Tilley on similar phenomena in Perthshire and elsewhere.[1] The case of the intrusion of the Skiddaw granite into the Skiddaw Slates as described by the present writer, is in complete agreement with the conclusions of these authors. In all these cases the conditions were such that the pressure-factor can be eliminated, and the system may be treated as involving only a rise of temperature due to the intrusion of an igneous rock.

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[1] Vernadsky, *Bull. Soc. Franç. Min.*, vol. xii, 1889, p. 447, and vol. xiii, 1890, p. 256.

In an elaborate discussion of the subject Goldschmidt points out that the data derived from the study of silicate melts have not much bearing on processes occurring in metamorphism, since in the latter case there is nothing approaching a liquid condition. It has been commonly assumed that reactions among the mineral constituents are carried on by means of small quantities of some solvent, presumably water, but it has been shown that some oxides can react in a dry state at temperatures far below their melting points in any form of combination. In all probability only a very minute fraction of the rock-constituents are in a condition to react at any given moment, but in course of time the whole rock can be transformed, and the resulting rock-types naturally arrange themselves in a zonary fashion around the intrusion, the individual zones not usually showing definite boundaries, provided there is no abrupt change in the original character of the rocks affected. Of course this does in reality often occur, and disregard of this factor has vitiated some of the older theoretical discussions founded on field-work. But if conditions are sufficiently uniform, the boundaries of these zones are isotherms.

Goldschmidt takes as a typical case a rock consisting mainly of Al_2O_3, CaO, MgO and SiO_2, which may be represented by the reversible equilibrium equation :

$$\underset{\text{Andalusite.}}{Al_2SiO_5} + \underset{\text{Diopside.}}{CaMgSi_2O_6} \rightleftharpoons \underset{\text{Anorthite.}}{CaAl_2Si_2O_8} + \underset{\text{Enstatite.}}{MgSiO_3}$$

The equilibrium at the higher temperatures here lies on the right. Only at one temperature and pressure, the transition point, can all four minerals exist in equilibrium.

Concerning this equation, if pressure is disregarded the Phase

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[1] Goldschmidt, *Die Kontaktmetamorphose im Kristianiagebiet, Vidensk-Selsk. Skrifter*, M. N. Kl., No. 1. Kristiania, 1911. Rastall, *Quart. Jour. Geol. Soc.*, vol. lxvi, 1901, pp. 116–140. Tilley, *Geol. Mag.*, vol. lx, 1923, pp. 101–107, vol. lxi, 1924, pp. 167–171, vol. lxii, 1925, pp. 363–367, *Quart. Jour. Geol. Soc.*, vol. lxxx, 1924, pp. 22–70.

Rule enables us to say that except at the invariant point the following ten mineral groups may exist at different temperatures :

1. Andalusite–diopside.
2. Diopside–anorthite.
3. Anorthite–enstatite.
4. Enstatite–andalusite.
5. Enstatite–diopside.
6. Andalusite–anorthite.
7. Andalusite–diopside–anorthite.
8. Andalusite–diopside–enstatite.
9. Anorthite–enstatite–andalusite.
10. Anorthite–enstatite–diopside.

For these groups the following relations are deducible from the Phase Rule :

(*a*) If combinations containing both andalusite and diopside are stable below the transition point, those containing both anorthite and enstatite are stable above it :

(*b*) The position of the transition point is independent of the nature of the solvent present, if any, provided that the solvent does not enter into solid solution with any of the phases.

As to which of the minerals shall appear or disappear at a given change of temperature the Phase Rule gives no *à priori* information : this must be determined empirically, and depends on the sign of the heat-effect at the transition point, as follows from the law of van't Hoff and Le Chatelier.[1]

However, the case is not usually so simple as this, because the components are not as a rule present in exactly the proportions to fit a double decomposition equation of this type : there may be excess of silica or of alumina, as well as of lime or magnesia. Hence we may find in such a rock quartz, olivine (forsterite), cordierite, spinel, corundum or periclase. Forsterite and periclase belong to the highly magnesian rocks, treated in a later section, but the occurrences of corundum, cordierite, spinel and quartz have to be considered here.

It was long ago shown by Morosewicz[2] that it is impossible for quartz and corundum to separate from the same melt. They invariably form aluminium silicates up to the limit of the silica present, and only alumina above the ratio $Al_2O_3 : SiO_2 = 1 : 1$ can form corundum. Similarly spinel and quartz are incompatible, cordierite or some other complex silicate forming instead. The conclusion to be drawn from all this is that aluminous silicates are the compounds stable at high temperatures and that, so far as we can see, the reaction

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[1] Goldschmidt, *op. cit.*, p. 126.

[2] Morosewicz, *Tschermaks Mitth.*, vol. xviii, 1898.

$$Al_2O_3 + SiO_2 = Al_2SiO_5$$

is not reversible.

The thermal relations of the three-component system $MgO–Al_2O_3–SiO_2$ in metamorphic rocks have been treated in a comparatively simple fashion by Dr. Tilley.[1] His discussion includes also a certain number of rock-types which belong more properly to the category of magnesian-carbonate rocks of a later section, but they are included here for the sake of brevity and convenience.

Omitting certain rare minerals of uncertain origin, as well as the pure magnesia-garnet, pyrope, which does not seem to exist in nature, Dr. Tilley recognizes eight minerals as appearing as phases in dry-melt investigations. With this restriction it is possible to represent this system by a triangular diagram, in which all the minerals except one appear as points on the sides of the triangle (Fig. 56). The triangle is then divided up into seven fields, representing the following three-phase assemblages.

1. Cordierite–quartz–enstatite.
2. Cordierite–quartz–sillimanite.
3. Cordierite–sillimanite–spinel.
4. Cordierite–spinel–forsterite.
5. Cordierite–enstatite–forsterite.
6. Periclase–spinel–forsterite.
7. Corundum–spinel–sillimanite.

In artificial melts $MgSiO_3$ crystallizes as clinoenstatite, and in natural rocks sillimanite is often replaced by andalusite, but these differences are of no importance ; they indicate solid inversions, which may here be disregarded. The natural occurrences of mullite may also be ignored.

All, or nearly all, of these assemblages have been found in metamorphic rocks, and one point that deserves special attention is that this diagram gives a simple and rational explanation of the very common occurrence of cordierite. It will be noted that this mineral is found in five of the seven possible assemblages.

In nature, however, other components are always present in addition to these, and there is no doubt that they have a great influence in changing the shapes of the fields of stability and perhaps in introducing new triple points, apart from the existence of other and definite compounds containing them. Thus for example in Perthshire Dr. Tilley has found rocks consisting of corundum–cordierite–M_2SiO_3 and corundum–cordierite–spinel. These are alternatives to points within fields 3 and 7 of Fig. 56, and represent shifts of equilibria due to special causes, analogous to the binary reaction represented by the equation on p. 139. Further, the presence of iron compounds and the possibility of the vicarious replacement of magnesia by ferrous iron has always to be considered. It seems probable that when there is a good deal of iron staurolite may be formed instead of cordierite, although there is some evidence that staurolite may be a stress-mineral, since it is often found along with kyanite.

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[1] *Geol. Mag.*, vol. lx, 1923, pp. 101–107.

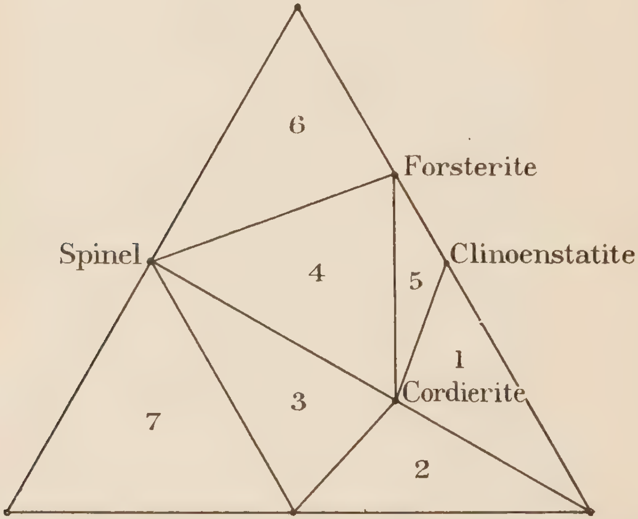

Fig. 56.—The system periclase–corundum–quartz : the mineral-assemblages in natural rocks.

(Tilley, *Geol. Mag.*, vol. lx, 1923, p. 106.)

In very many instances of metamorphic clay-slates, of which the Skiddaw aureole may be taken as a typical example,[1] both felspars and micas are abundant. It is probable that the occurrence of these flux-minerals is largely due to the presence of water or other mineralizing agents, either originally present in the rocks, or derived from the intrusive magma. The micas include muscovite and its soda analogue, as well as biotite and phlogopite, and among the felspars are both orthoclase and plagioclases near

[1] Rastall, *Quart. Jour. Geol. Soc.*, vol. lxvi, 1910, pp. 116–140.

the albite end of the series. None of these are normally formed in the dry way. The rocks nearest to the Skiddaw granite are so rich in biotite as to be commonly called mica-schist. In this aureole both andalusite and cordierite are extremely abundant.

Calcareous Rocks. The treatment of this category is specially easy and satisfactory, for two principal reasons. In the first place the composition of the rocks themselves is very simple, often approaching very closely to a system of one component, $CaCO_3$ (or as some writers prefer to state it, $CaO + CO_2$, as two components): secondly the chemical and physical behaviour of the rock-constituents is well known and almost free from complications. The usual impurities in the calcareous rocks are clay and sand, or to put it otherwise, Al_2O_3 and SiO_2. An important distinction arises as to whether MgO is or is not abundant, i.e. whether the rock is dolomitic or not. The dolomitic rocks in the broad sense show some very interesting features and need separate treatment.

Considering first the case of a nearly pure limestone like the Chalk, when subjected to thermal metamorphism, the simple equation

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

is applicable. When chalk is burnt in an open kiln the reaction proceeds towards the right to completeness, yielding lime, but in a closed space the partial pressure of the CO_2 stops the dissociation and the equilibrium lies on the left. Now in underground metamorphism the CO_2 cannot escape and the only thing that can happen is crystallization of the calcium carbonate. Under such conditions aragonite always inverts to calcite, and the result is a mass of more or less coarsely crystalline calcite, forming a pure marble. The best statuary marbles are those of the finest grain, and may be described as "sugary." Such are the marbles of Carrara in Italy and Pentelikon in Greece. Such marbles of varying grain are extremely common in many localities. It must, however, be remembered that a very similar effect is produced by dynamic metamorphism of pure limestones, the resulting marble often showing very little outward sign of pressure, since, as shown by experiment, calcite rocks "flow" very readily.

It seems to be clear that in such cases of the complete reconstitution of a rock by crystallization without any true chemical reactions, the effect is mainly produced by solution, the solvent being partly the natural moisture of the rock, and partly no doubt liquids or vapours introduced by the intruding igneous rocks. Thus the whole process of metamorphism in a pure limestone is of a physical nature.

On the other hand, when impurities are present in the limestone clean-cut chemical reactions take place resulting in the formation of a variety of secondary minerals. The simpler cases are easily reduced to definite equations. Nevertheless one puzzling feature is common to all these reactions, namely that the $CaCO_3$ reacts readily with other constituents, the reaction sometimes going on to completeness, although the CO_2 is not free to escape. It is not at all clear what becomes of it. This is shown by the extremely simple and common reaction

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

which occurs when an impure sandy or cherty limestone is metamorphosed. The result is the formation of the simple lime-silicate, which in nature always crystallizes as the monoclinic pyroxene wollastonite, though artificial $CaSiO_3$, formed by heating lime and quartz, always forms a hexagonal mineral, pseudo-wollastonite. Now the inversion point of the two forms is known to be 1190°, hence it follows that the metamorphic process is carried out in the presence of some flux, which lowers the freezing point below the inversion point. This clearly shows the important part played by solvents, doubtless mainly water, in such reactions, as mentioned above, since wollastonite cannot be formed in the " dry " way.

Lime and silica can combine in two ratios, as $CaSiO_3$ and Ca_2SiO_4. However the last-named, monticellite, is not a common mineral. It has been observed in limestones at Vesuvius (Mte. Somma); on Mte. Monzoni, Tirol; and at Magnet Cove, Ark., but under ordinary conditions the result of an excess of $CaCO_3$ over SiO_2 is the formation of wollastonite and calcite, i.e.

$$2CaCO_3 + SiO_2 = CaSiO_3 + CO_2 + CaCO_3;$$

this is curious, since the corresponding magnesium orthosilicate forms very readily, as will appear later.

When alumina is present in addition to silica we have a system of three components, $CaO–Al_2O_3–SiO_2$. This system is one of enormous practical importance in connection with blast-furnace and other slags, and especially in the manufacture of Portland cement. It has therefore been studied very thoroughly but unfortunately some of the conclusions formerly accepted have been upset by the recent discovery of mullite (see p. 137). All the details of this experimental work will not be discussed here, partly because several of the artificial compounds there obtained are not known as natural minerals, and partly because certain minerals, especially those of the garnet group, so common in metamorphic limestones, are not found in artificial melts at atmospheric pressure. Hence the work on this system, so useful for industrial purposes, has not thrown as much light as might have been hoped on the problems of geology.

The petrographical study of a large number of metamorphosed impure limestones has shown that the commonest three-component minerals are garnet, vesuvianite and lime-felspar. In this case the determining factors are possibly in part the actual proportions in which the different components are present, but it is clear that physical factors are also of first-rate importance. Lime felspar (anorthite) can easily be made from a dry melt, by the simple fusion of its constituents in the correct proportions: its formation therefore does not depend on fluxes and it is a low-pressure mineral. On the other hand garnet cannot be made from such melts, and its high density shows that it is a high-pressure mineral. Analyses of vesuvianite (idocrase) show that it contains the OH group or fluorine and it is therefore a pneumatolytic mineral, only formed in the presence of fluxes. The very common occurrence of garnet in metamorphic limestones shows that in most cases pressure is high.

It is quite easy to construct an equation to show the formation of a wollastonite-garnet rock from an argillaceous sandy limestone or calcareous shale, a very common rock-type. As an example this might take the following form.

$$4CaCO_3 + Al_2SiO_5 + 3SiO_2 = \underset{\text{Wollastonite.}}{CaSiO_3} + \underset{\text{Grossularite.}}{Ca_3Al_2Si_3O_{12}} + 4CO_2$$

This of course is only an ideal case, and there may be endless variations in detail: there may be excess of calcite or excess of silica (quartz). If the aluminium silicate is hydrated (e.g. kaolin) idocrase might be formed instead of garnet. Actual examples of such rocks are too numerous to be referred to in detail.

Although the presence of alumina in limestones without silica is rare, nevertheless it is known to occur in one or two localities. The alumina may here have been derived from the disintegration of bauxitic rocks, which are free from silica, and not from ordinary clays. When such an aluminous limestone is metamorphosed, no chemical reaction occurs, as compounds of lime and alumina are not found in nature, though several artificial ones are known. The $CaCO_3$ crystallizes as calcite and the Al_2O_3 as corundum, which in its gem-form is known as ruby or sapphire according to colour. This appears to be the origin of the rubies of Burma, which are found embedded in coarse-grained white marble.[1]

A special case arises when the igneous intrusion itself gives off fluxing vapours, especially fluorine and boron. This comes under the heading of pneumatolysis. If fluorine is dominant, the obvious effect is the formation of fluorspar, CaF_2, and this has undoubtedly taken place to a large extent in many places, especially in connection with ore-formation, as for example in Derbyshire and Cumberland, in the Carboniferous limestone. Somewhat less common, though still widespread, is the reaction of boron vapours on impure limestones, giving rise to axinite, danburite and datolite. The first-named is well known in the metamorphic aureoles of the granites intruded into calcareous Devonian sediments in Cornwall (St. Austell and Bodmin Moor granites).[1] These minerals are often associated with actinolite, idocrase, epidote and garnet of rather peculiar characters, these also probably carrying a certain amount of boron, fluorine or OH.

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[1] Crystalline corundum, as sapphire, etc., is also formed by crystallization of absorbed alumina from igneous rocks.

Magnesian Carbonate Rocks. The thermal metamorphism of the magnesian limestones, both pure and impure, is a subject of great interest, and the facts are pretty well known, some instances having been very thoroughly studied. The behaviour of the mineral dolomite when heated differs somewhat from that of calcite, as shown by careful investigations carried out in connection with basic steel furnaces. The ordinary open-hearth basic steel furnace is lined with the so-called "shrunk dolomite" which is simply burnt (calcined) magnesian limestone. During this calcination the dolomite dissociates in two stages, thus

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2 \quad . \quad . \quad (a)$$

On further heating all the CO_2 is driven off, resulting in a mixture of lime and magnesia: in each stage there is a decrease of volume, hence the use of the term "shrunk."

The point of interest here is that equation (*a*) also represents exactly what happens in the thermal metamorphism of a pure dolomite rock.[2] The $CaCO_3$ crystallizes as calcite, the MgO forms a cubic mineral known as periclase. This mineral, however, is unstable in the presence of water and nearly always undergoes hydration to brucite $Mg(OH)_2$. The first analyses of such rocks happened to be carried out on specimens derived from very pure dolomite rocks in the Tyrol and therefore showed a nearly constant composition, and it was believed that this white granular marble-like aggregate was composed of a simple mineral of the composition $CaCO_3.Mg(OH)_2$: this was called predazzite or pencatite. But later microscopic examination revealed the composite character and the rock is now known as brucite-marble. The process is known as *dedolomitization.*[1]

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[1] Barrow and Thomas, "On the Occurrence of Metamorphic Minerals in Calcareous Rocks in the Bodmin and Camelford areas, Cornwall." *Min. Mag.*, vol. xv, 1908, pp. 113–123.

[2] Even the purest dolomite rocks generally contain calcite as well as dolomite, but this of course makes no difference in the reaction, except in the ratio of CaO to MgO, which is greater than 1 : 1 in the final product.

When siliceous dolomites are calcined various silicates are formed, according to the proportions in the rock, and the same thing happens in metamorphism. From petrographical study of actual instances it is clear that two cases present themselves, (1) when dolomite is in excess; (2) when silica is in excess. These two cases can be represented by the following equations:

$$2CaMg(CO_3)_2 + SiO_2 = Mg_2SiO_4 + 2CaCO_3 + 2CO_2 \quad . \quad (b)$$
$$CaMg(CO_3)_2 + 2SiO_2 = CaMgSi_2O_6 + 2CO_2 \quad . \quad . \quad (c)$$

In the first case the result is forsterite and calcite (forsterite-marble); in the second case diopside-rock.[2] The magnesium silicates, especially the forsterite, often undergo serpentinization, resulting in a streaky green and white rock called Connemara Marble [3] or ophicalcite.

Ophicalcite often shows a remarkably regular banded structure, which has been supposed to be an organism, and has even been named *Eozoon canadense.* It was supposed to be a gigantic foraminifer, but since this structure has been observed, among other places, in blocks of metamorphosed dolomite, ejected from the old crater of Vesuvius (Monte Somma) it is clear that it is of purely physical origin. It must be referred to rhythmical precipitation from solutions, of the type described by Liesegang.[4]

This opens up a very important and interesting question, namely, the extent to which diffusion takes place across the boundary between igneous intrusives and the invaded rock. So far very little attention has been paid to this subject, but it is clear that such diffusion does take place. A very interesting case has been described from Port Shepstone in Natal, where by earth-movement a granite dyke invading a dolomite rock has been broken up into blocks, isolated in the dolomite and later subjected to thermal metamorphism. The dolomite rock itself is a particularly pure coarse-grained white marble; a block of granite of about 3 feet in diameter was surrounded by a series of shells of silicate minerals, a striking feature being that the successive shells of silicates showed a lower percentage of silica at greater distances from the margin. The innermost shell consisted of nearly pure diopside and the outermost was a normal ophicalcite derived from forsterite-marble: that is to say these shells corresponded exactly to the equations (*b*) and (*c*) above. The intermediate rings showed magnesia-mica and other minerals indicating that alumina also diffused from the granite, though not so far as the silica.[1]

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[1] Teall, *Geol. Mag.*, 1903, p. 513. Harker, *The Tertiary Igneous Rocks of Skye.* Mem. Geol. Survey, 1904, pp. 144–151.

[2] See Teall and Harker, *loc. cit*: also Hatch and Rastall, *Quart. Journ. Geol. Soc.*, vol. lxvi, 1910, pp. 507–520. Du Toit, *ibid.*, vol. lxxv, 1919, pp. 119–137.

[3] Cronshaw, *Geol. Mag.*, vol. lx, 1923, pp. 467–471.

[4] Liesegang, *Geologische Diffusionen*, Dresden, 1913, pp. 81–106.

When alumina alone is present in a magnesian carbonate rock it combines with the magnesia, forming spinel, thus

$$CaMg(CO_3)_2 + Al_2O_3 = CaCO_3 + MgAl_2O_4 + CO_2 \quad . \quad . \quad . \quad (d)$$

An example of this reaction was also seen at Port Shepstone, in the form of a rounded patch of pink spinels embedded in crystalline dolomite.

More commonly however alumina is accompanied by silica, as clay-substance; a simple case can be represented by combining equations (*b*) and (*d*), thus:

$$\begin{array}{ll} 2CaMg(CO_3)_2 + SiO_2 & = Mg_2SiO_4 + 2CaCO_3 + 2CO_2 \\ CaMg(CO_3)_2 + Al_2O_3 & = MgAl_2O_4 + CaCO_3 + CO_2 \\ \hline \multicolumn{2}{l}{3CaMg(CO_3)_2 + Al_2O_3 + SiO_2 = Mg_2SiO_4 + MgAl_2O_4 + 3CaCO_3 + 3CO_2} \end{array}$$

which is a spinel-forsterite-marble. Such a rock has been described by Clough and Pollard from Glenelg, Scotland.[2]

Very commonly however the result of the metamorphism of such argillaceous dolomites is the formation of magnesia-mica on a large scale (phlogopite if free from iron, biotite if a little iron is present). It is obvious that this type grades imperceptibly into the metamorphism of argillaceous rocks, of the calcareous shale type, as already described, and the subject need not be pursued in detail, but reference may be made to *cipollino*, a type of marble rich in mica, found in many areas of crystalline schists. Now all micas contain either the OH group or fluorine, or both, and the presence or absence of high-pressure water and fluorine obviously determine whether the reaction shall proceed according to the simple equations given above or whether more complicated minerals shall be formed, such as micas, chondrodite, humite, and others. In some instances the presence of chlorine gives rise to scapolite.[3]

Here again, as in the non-magnesian limestones, we encounter the formation of garnets on a large scale: since, however, garnet is known to be a high-pressure mineral, for the sake of brevity this part of the subject may be relegated to the section on dynamic metamorphism.

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[1] Hatch and Rastall, *loc. cit. supra.* du Toit, *Quart. Jour. Geol. Soc.*, vol. lxxv, 1919, pp. 119–137.

[2] Clough and Pollard, *Quart. Jour. Geol. Soc.*, vol. lv, 1899, pp. 372–379.

[3] Note: minerals of the scapolite group are also often formed from plagioclase felspar by pneumatolysis (see p. 131).

Ferruginous Rocks. When a small amount of iron is present in the siliceous and aluminous types just described it enters into isomorphous mixture in the silicates, forming green or black pyroxenes, green olivine instead of colourless forsterite, and so on, but silicates with a high percentage of iron are not formed readily. A more common result is the formation of magnetite, or sometimes hæmatite, though the last named is more common in pressure rocks (hæmatite-schists). Thus a siliceous ironstone would crystallize as magnetite and quartz rather than as iron silicate.

The study of certain ores of zinc and manganese has suggested that they have been formed by processes analogous to dedolomitization in the broad sense, as above described. Thus the zinc ores of Franklin Furnace, New Jersey, contain some very interesting minerals. The ore consists mainly of zincite, ZnO ; franklinite, a zinc-manganese spinel ; willemite, Zn_2SiO_4, with calcite and rhodochrosite, $MnCO_3$. The analogy with brucite and forsterite marbles is here obvious. Again some of the manganese ores of India and Brazil contain manganese-pyroxenes, a manganese-olivine (tephroite), manganese-garnets, and so forth. In these cases the zinc and manganese seem to play the same parts as the magnesium in dolomite rocks. The workable ores of manganese are various oxides and hydroxides formed by the oxidation of these minerals near the surface, but in depth the ores pass into silicates.[1]

Dynamic Metamorphism. We must now pass on to consider those forms of metamorphism in which pressure is the dominant factor. Here, however, it is necessary to repeat once more that it is impossible to visualize such a condition that pressure alone is operative, without an accompanying rise of temperature. This is brought about in two ways : doubtless to an important but unknown extent as the result of mechanical friction, and also, as pointed out by Dr. Harker,[2] owing to the fact that pressure reactions in minerals are exothermic. The total amount of heat-energy from these two sources may be and probably is very considerable.

It is very important at this point to emphasize once more the fact that in dynamic metamorphism two kinds of pressure are operative, and that these may have quite different, and indeed opposite effects on chemical reactions and physical changes of state. For example : in the ordinary course it is clear that uniform or " hydrostatic " pressure in nearly all cases raises the melting point of minerals. It has been shown that differential pressure or "stress" has a precisely opposite effect and to a much higher degree.[1] Hence stress must greatly facilitate the formation of new minerals by reactions between the existing constituents of the rock. Probably the effect of simple hydrostatic pressure is very small, as stated by Dr. Harker, and "we may without serious error consider metamorphism as controlled by the two factors temperature and shearing stress."[2] Apparently the one and only factor of mineral formation which is not altered by stress is the temperature of inversion of enantiotropic forms: this seems to remain constant under all conditions.

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[1] For a discussion of these cases, with references to the literature, see Rastall, *The Geology of the Metalliferous Deposits*, Cambridge, 1923.

[2] Harker, *Proc. Geol. Soc.*, Feb. 15, 1918. Pres. Add. p. lxvii.

Nevertheless it is obvious that on the whole high pressure of whatever kind must favour the formation of minerals of high density and small specific volume in accordance with the principle of Le Chatelier. Among the distinctively stress-minerals, as enumerated by Harker, are sericitic mica and the chlorites, albite, epidote, and zoisite, amphiboles as opposed to pyroxenes, kyanite, staurolite, chloritoid and talc, hæmatite and rutile. However, it is important to notice that the volume-law does not always apply, since the amphiboles have a larger specific volume than the corresponding pyroxenes of the same composition. Some other factor here comes into play. The minerals of the garnet group have a small specific volume and they are specially characteristic of crystalline schists and deep-seated rocks in general.[3]

Another point that arises from empirical observation is the common occurrence in dynamic metamorphism of minerals having a general platy, flattened and bladed habit, such as micas, chlorites, kyanite and the amphiboles. The crystals of these minerals, in conformity with ordinary laws of dynamics, naturally tend to arrange themselves with their long axes or tabular surfaces at right angles to the direction of pressure: it is only certain specially "strong" minerals, such as the garnets, that manage to maintain their normal equidimensional forms in spite of the pressure. From this point of view quartz is a "weak" mineral, and is generally found in platy or granular aggregates, drawn out in a direction at right angles to the pressure, as may be seen in many gneissose rocks and in sheared quartzites. This general weakness of quartz also expresses itself in a disturbance of the optical properties, giving rise to the so-called *strain-shadows* (undulose extinction).

It is not proposed here to enter into a detailed consideration of the categories of dynamically metamorphosed rocks, either from the point of view of structures, of mineral composition, or of the origin of the various types met with in nature. A systematic treatment will be found in a multitude of geological textbooks, and in various special works devoted to this side of the subject.

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[1] Boeke, *Grundlagen der phys.-chem. Petrographie*, 1915, pp. 22–30.
[2] *loc. cit.*, p. lxxiii.
[3] Fermor, *Rec. Geol. Surv. India*, vol. xlii, 1913, pp. 41–47.

In general studies of the crystalline schists one point that stands out with perfect clearness is that they have been derived from original rocks of all kinds, both igneous and sedimentary. In very many cases it is possible to determine from the constituent minerals what the original character of the rocks may have been : thus when schists are found to be rich in silicates of alumina (kyanite, sillimanite), or certain more complex silicates rich in alumina, it is a fair inference that they were originally sediments, since no known igneous rocks contain sufficient alumina to give rise to these minerals. Further another large group of minerals arise from the pressure metamorphism of limestones and dolomites. On the other hand certain large groups, such as the micas and the felspars, can originate from rocks of almost any kind. It we consider such a pair of primary rocks as an arkose and a granite, we see that the chemical difference between them may be very small, and on *a priori* grounds, it may be very difficult or impossible to say whether a certain gneissose rock has been derived from one or the other.

Metasomatism. The geological processes summed up under the general category of metasomatism differ from metamorphism mainly in the fact that an alteration in the final bulk composition of the rock is involved ; sometimes merely addition of material, sometimes a complete replacement. Several of the more important of these processes are referred to elsewhere in this book, and this section will consist to a large extent of cross references to other chapters, in order to avoid repetition. It is obvious that there must be a great many geological processes accompanied by change of chemical composition, and the definition might be very widely extended, but only a few of the more important examples will be mentioned.

It is customary to make a distinction between processes of metasomatism taking place at high temperatures and pressures, that is under metamorphic conditions, and those that go on at the ordinary temperature at or near the surface of the earth, but this distinction is rather difficult to maintain in practice, and a classification will not be attempted here.

Metasomatic Changes in Limestones. It is well known that calcareous rocks are more susceptible to chemical alteration than any other group, owing to the higher solubility of the carbonates as compared with most other rock-forming minerals. Consequently they provide some of the best examples of metasomatism. One of the most important and wide-spread of these is dolomitization, which is dealt with pretty fully in Chapter IX (pp. 193–196). Another instance, of the highest economic importance, is the formation of workable deposits of iron ore, sometimes on a very large scale, by replacement of limestones by iron compounds. In some instances this mode of origin of iron ores, though often suggested, is not fully proved, as in the case of some oolitic ironstones, but there are many occurrences in which there is no manner of doubt of the correctness of this explanation. Among these the hæmatite ores of Cumberland and Furness, the Forest of Dean, and the Bilbao district in Northern Spain may be mentioned. In Cumberland and Lancashire it is quite clear that the original Carboniferous limestone has been replaced by iron compounds derived from solutions percolating through from the overlying very ferruginous red rocks of the Permian and Trias. The replaced masses occupy just the positions they should do if the flow of these solutions were controlled by joints, fault-planes, impervious strata and so on. However the exact nature of the chemical processes that went on is not clear: it is still uncertain whether the calcium carbonate was first converted to ferrous carbonate (siderite) or whether it went direct to ferric oxide. Another point still needing explanation is why the iron mineral is the anhydrous hæmatite, and not some form of hydrate.

In the Spanish deposits, which were formed by replacement of a limestone of Upper Gault age, there is a good deal of siderite, suggesting alteration in two stages: first carbonate replacement, followed by oxidation.

Limestones are also very liable to a process of silicification, resulting in the formation of *chert*. Here the whole or part of the calcium carbonate has been bodily replaced by silica, usually not quartz, but some form of chalcedonic or opaline silica. The resulting rock, which is sometimes quite black, is very like flint. The process of replacement is evidently a "molecular" one, to use a rather vague term, since the most minute details of rock-structures or fossils are often very perfectly preserved, and there is no question of bodily removal, with subsequent filling of the cavity. The source of the silica is often rather obscure. It is very generally attributed to the remains of siliceous organisms, sponge-spicules and so on. In some instances this is undoubtedly correct, but in others it appears quite inadequate. It has been suggested that the silica may have been derived from magmatic solutions poured out during the later stages of submarine eruptions, but this requires further proof.

Another very peculiar case is that in which limestone has been converted to masses of calcium phosphate. This needs exceptional circumstances, which are best realized where coral islands have been covered by deposits of guano, as in Christmas Island in the Indian

Ocean to the south of Java. The chemistry of this process is too obvious to need elaborate description.

There exist in geological literature innumerable descriptions of the development of silicate minerals in limestones and dolomite rocks as a result of contact metamorphism. In such cases it is nearly always assumed that the altered rock was originally "impure," that is, that it already contained silica, alumina and so on. Often this was undoubtedly so, but not always. It is perfectly clear that in some instances there has been diffusion of magmatic solutions into the limestone, producing a zone of silicate rock along the junction. An example from Natal is described in an earlier section of this chapter (p. 147) and a similar cause accounts for many instances of the so-called "Skarn" rocks, which are often associated with valuable ore-deposits. This kind of thing approaches very closely to certain types of pneumatolysis.

In the case of many non-ferrous ore-deposits, and especially among the sulphides, there has been much dispute as to whether they originated by direct magmatic intrusion, or from replacement of older rocks by metalliferous solutions. A large literature has already accumulated on the origin of those great masses of pyrite that are of fundamental importance in industrial chemistry as sources of sulphuric acid, while some of them yield also much copper and nickel. Some of them have been attributed to direct intrusion of sulphidic magmas, derived from basic silicate magmas by differentiation, but there is now a tendency to return to the older view that the sulphide masses have been formed by the replacement of already existing rocks through the agency of aqueous solutions, these solutions being possibly of ultimate magmatic origin.[1] Hardly any one now believes that large-scale ore-deposits are due to replacement by the circulating waters of the upper crust, of meteoric origin. Only in a few exceptional instances is this view still held, such for instance as the great lead-zinc deposits of Missouri, which some writers think may have been shifted laterally in solution for a few miles, from an older deposit connected with igneous rocks.

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[1] Gregory, J. W., *Trans. Faraday Soc.*, vol. xx, 1925, pp. 449–458, with references and discussion.

CHAPTER VIII

THE PHYSICAL CHEMISTRY OF ROCK-WEATHERING

Nature of Weathering. The decomposition of rocks under the influence of the ordinary agents of weathering, rain, frost, changes of temperature and wind, is due to a complicated series of processes which are, however, for the most part of a physico-chemical nature. Some of these agents are purely physical in their nature, while others are mainly chemical, but it is only rarely that the effects produced are due to one cause alone : much more commonly they are the result of a combination of different processes acting together. It will be well to begin with a very brief summary of the different categories of geological agents of rock destruction. Among the more purely chemical agencies we may place solution, hydration, oxidation and reduction, hydrolysis and the action of acids and other chemical compounds. Most of these processes take place in the presence of water : in fact chemical weathering is characteristic of regions of moist climate and is naturally more active at a high temperature. It therefore reaches its maximum in the tropics. Among the chief physical agencies are the expansion of water in freezing, expansion and contraction of the rocks themselves and of their component minerals on change of temperature, and the mechanical effect of wind-borne solid material. The water-circulation in the rocks is also a result of physical causes, along with its attendant phenomena of capillary rise of the solutions and other minor effects. The possible effect of bacteria in rock-decay is a question still in need of investigation and nothing definite can yet be said on this subject, which may, however, eventually prove to be of great importance.

It is perhaps scarcely necessary to point out that minerals vary widely in their resistance to the solvent action of water and to chemical agents in general, as well as to physical changes. But it is important to remember that for this reason, most rocks being aggregates of different minerals and not homogeneous, weathering is usually more or less differential. Further there comes in here the general question of stability of minerals under the conditions existing in rocks at and near the surface. The intrusive igneous rocks for example have been formed at temperatures and pressures certainly higher than those prevailing at the surface, and there can be no doubt that some of their minerals are actually in a state of unstable equilibrium, and therefore will the more readily undergo changes. On the other hand the minerals newly formed in sediments must necessarily be those adapted to the prevailing equilibrium conditions at and near the surface, and therefore they should be more stable. The glassy parts of all lavas must necessarily be unstable and this is perhaps the reason why lavas break down so readily to fertile soils.

The general principles involved in this part of the subject can perhaps be most conveniently illustrated without unnecessary waste of space by taking a few concrete examples and treating them in some detail. Since the felspars together form one of the most widely distributed and abundant mineral groups, they will be taken first.

The Weathering of the Felspars. Since the members of this group vary a good deal in composition they naturally show a corresponding variation in their decompositions. The most natural division is into two groups, the potash-felspars and the plagioclase series.

In the potash-felspar group orthoclase and microcline have exactly the same chemical composition, $K_2O.Al_2O_3.6SiO_2$. (Both varieties always as a matter of fact contain a certain proportion of the albite molecule, but this may be ignored for the present.) This compound may be regarded either as a double silicate of potash and alumina, or as the potash salt of an alumino-silicic acid. Potassium alumino-silicate is a salt composed of a very strong base and a weak acid: it is therefore very liable to hydrolysis. The consequent reaction may be expressed by the following equation:

$$K_2O.Al_2O_3.6SiO_2 + 3H_2O = 2KOH + Al_2O_3.2SiO_2.2H_2O + 4SiO_2$$

The products on the right-hand side therefore consist of caustic potash, which is very soluble, free silica, and a hydrated silicate of alumina, which when crystalline is called kaolinite, and when impure and amorphous is the chief constituent of clay. The potash is removed in solution: the silica is probably set free in the colloidal form and not as quartz: some of it may combine with the potash to form a soluble potassium silicate. Hence the residual product of complete hydrolysis of a potash-felspar is a mass of clay-substance, which when pure white is called china-clay or pipe-clay.

Many geological writers, especially those of the older school, attribute this process of kaolinization to the action of carbon dioxide dissolved in the ground-water. The equation then becomes as follows :

$$K_2O.Al_2O_3.6SiO_2 + CO_2 + 2H_2O = \\ K_2CO_3 + Al_2O_3.2SiO_2.2H_2O + 4SiO_2$$

It is impossible at present to say definitely which of these explanations is the correct one : probably both apply in different cases and the point is of no real importance, as the final residual and insoluble product is the same.

In many places, especially where there is evidence of volcanic or solfataric action (hydrothermal conditions) it is found that potash-felspar has been largely converted into an aggregate of white mica. This can be expressed by the following rather less determinate equation, in which it is necessary to introduce an unknown factor x.

$$K_2O.Al_2O_3.6SiO_2 + xH_2O \rightarrow xKOH + (H,K)_2O.Al_2O_3.2SiO_2 + 4SiO_2$$

Here it is assumed that in muscovite hydrogen and potash are present in an indefinite ratio : this seems to fit the facts best, although some writers assign to muscovite the complicated formula $H_2O.3K_2O.4Al_2O_3.8SiO_2$. There is little evidence in support of this and the hydrogen is almost certainly present as the OH group and not as H_2O. This process of sericitization of felspar is very common under such conditions as give rise to the formation of ore-deposits : it is, for example, an almost universal accompaniment of the gold-silver lodes of the Tertiary lavas both in Europe and western America. It appears to be a more or less superficial phenomenon and therefore comes within the category of weathering. It is also very commonly observable in rocks that have apparently been weathered under normal conditions.

Everything that has just been said with regard to potash-felspar applies equally to pure albite, with the substitution of soda for potash in the equations and in the text. In an earlier chapter a discussion has been given of the constitution of perthite, which is shown to be a mechanical mixture, due to the unmixing of two originally homogeneous solid solutions of the orthoclase and albite molecules. The results of weathering in perthite will of course be obvious to the reader, without any further elaboration.

The Plagioclase Felspars. Pure albite is, however, a rather rare mineral : the soda-felspar molecule mostly occurs in mixture or solid solution with the anorthite molecule as plagioclase. It is necessary therefore to consider now the behaviour of the last-named under weathering, the soda molecule giving rise to the products already mentioned, kaolinite or clay substance, and sericitic mica (paragonite), with soda instead of potash as in muscovite. The behaviour of the anorthite molecule is not quite so easy to reduce to a quantitative form, since its products seem to vary more widely under different conditions. Decomposed plagioclase rich in lime in very many cases certainly yields a good deal of calcite and also very commonly zoisite, and certain members of the chlorite group. A mixture of calcite, zoisite and more or less chlorite forms the opaque white, cream-coloured or greenish substance known as saussurite, which is so common in gabbros : it is uncertain to what extent this particular product is of hydrothermal origin. The more usual type of alteration of the anorthite molecule yields mainly a mixture of clay-substance and calcite, which may be represented by the following theoretical equation, though it must be admitted that this is mainly founded on guess-work and analogy.

$$CaO.Al_2O_3.2SiO_2 + CO_2 + 2H_2O = CaCO_3 + Al_2O_3.2SiO_2.2H_2O$$

The alteration of plagioclase to scapolite is here regarded as a pneumatolytic effect (see p. 131).

Bauxite. In any discussion of the decomposition of the alumino-silicates it is necessary to mention that peculiar type of weathering, so common in the tropics, which gives rise to the lateritic and bauxitic deposits. As we have seen, in temperate climates the weathering of the alumino-silicates, as exemplified by the felspars, yields hydrated aluminium silicates, such as kaolinite and micas. Under tropical conditions the process of chemical decomposition goes much further, the silica is also converted into a soluble form and removed, the resulting residual product being composed essentially of aluminium hydrates, which when fairly pure constitute bauxite, the common ore of aluminium. This is sometimes regarded as a mineral, the formula $Al_2O_3.2H_2O$ being assigned to it. In reality, however, it is a rock and is composed of a mixture of gibbsite, $Al_2O_3.3H_2O$ and diaspore, $Al_2O_3.H_2O$. Moreover it is probable that in some cases, if not in all, these aluminium hydrates are really present in the colloidal form and not as true crystalline minerals : they may then be regarded as alumina gels. (Compare the description of the hydrated iron oxides on p. 240).

Nepheline. The only member of the felspathoid group that is of importance as a rock-former is nepheline, and even this is limited in its distribution. Artificial nepheline, agreeing in all characters with the natural mineral, has been made, having the constitution $NaAlSiO_4$. Natural nepheline always contains more or less potash and deviates somewhat in other ways from this composition, probably owing to solid solution with other molecules ; possibly orthoclase or leucite and albite. Nepheline when decomposed can often be seen under the microscope to have passed more or less completely into an aggregate of white mica. This change from the chemical point of view is very slight, i.e.:

$$NaAlSiO_4 \rightarrow (H,Na)AlSiO_4.$$

That is to say a certain proportion of the sodium has been leached out and replaced by hydrogen.

In many descriptions of nepheline-bearing rocks mention is made of a supposed mineral cancrinite, to which a very complicated formula is assigned: one version of it is $H_6Na_6Ca(NaCO_3)Al_8(SiO_4)_9$. The writer regards this sort of thing as absurd, and believes that the so-called cancrinite is in reality a mechanical mixture of a soda-mica, calcite and perhaps other molecules: in fact in reality a pseudomorph after nepheline; the lime molecule being introduced from outside as $CaCO_3$ in solution in ground-water. A similar product has been obtained artificially by treatment of nepheline with sodium carbonate at a high temperature. The nepheline used in these experiments must have originally contained some lime, perhaps as the anorthite molecule, and this may also have been the case with some of the natural nepheline that has been altered to cancrinite, although the large proportion of $CaCO_3$ recorded in some analyses, up to 10 per cent., certainly suggests an introduction of calcium carbonate from outside.

Sodalite is very commonly classed with the felspathoids. It is quite clear that some sodalite is an alteration product of nepheline, and this may always be the case. Sodalite always contains chlorine up to 7 per cent., and this fact suggests that the alteration may have been brought about by the percolation of water from the sea or from salt lakes. In that case it is perhaps hardly weathering, but rather metasomatism.

The Mica Group. The common rock-forming micas divide themselves pretty clearly into two groups, the muscovite group and the biotite group. In strictness of nomenclature muscovite is a potash-mica, but there is a corresponding soda-compound, paragonite, of exactly analogous composition. There is no need to attempt to separate these here, as they both behave in exactly the same way, and may be conveniently called the white micas. White mica is a remarkably stable substance and resists chemical weathering to a high degree. Owing to its very perfect cleavage, it is rather easily broken up by physical processes. However white mica, more or less finely divided, is very common in sediments. As we have just seen white mica is also a common product of the weathering of felspars and other aluminous silicates, hence we must suppose that it is stable at low temperatures and pressures, as well as when first formed in deep-seated igneous rocks. If so, its field of stability is extraordinarily wide.

The biotite group or the brown micas on the other hand, are more complicated in composition and much less stable. In this group are to be included all those micas which contain both an alkali metal and either iron or magnesia, or both. As types of the two subsidiary groups we may select biotite, or potash-iron mica, and phlogopite, or potash-magnesia mica: there are, however, also varieties of each in which soda replaces more or less of the potash, although it is rather doubtful whether there are any micas of this class in which all or nearly all the alkali is soda. Potash is certainly dominant over soda. This point is of importance in connection with questions of soil-fertility, since potash is of much greater value than soda as a plant-food, and much more liable to be deficient in soils. Rocks rich in biotite, however, yield soils that are rarely deficient in potash, partly because this substance is naturally abundant in the rock and partly because biotite is very unstable and easily decomposed. The actual process of the weathering of biotite is still somewhat obscure. In the first place it is clear that the original brown biotite often undergoes a process of decoloration or bleaching, being converted into a white or pale mica, sometimes of a greenish colour. This process appears to be primarily at any rate a leaching out of the iron, which appears to exist in micas in both the ferrous and the ferric states. It can often be observed in microscopic sections of slightly weathered biotite-granites that the originally brown biotite has been converted wholly or partially into a greenish substance having the optical characters of chlorite. This seems to involve a removal of most of the iron, especially the ferric part, with retention of the magnesia and alumina, and addition of water: the alkalies being also removed. The constitution of all the minerals here concerned is so complicated and uncertain that no good purpose is served by an endeavour to represent the changes as equations. The changes that take place in micas of the magnesian type, i.e. phlogopite, are also mainly in the direction of the formation of some member of the chlorite group.

The Ferromagnesian Silicates. In this group are included all those silicates of magnesium, iron and lime, either simple or mixed, in which alumina is entirely absent or occurs only in insignificant amounts, probably in more or less accidental solid solution. There are here three principal groups, the amphiboles and the pyroxenes, both of which are metasilicates, and the olivine group, which are orthosilicates. Broadly speaking the metasilicates are more stable than the orthosilicates. All these groups are isomorphous series, or mixtures of different molecules in varying and indefinite proportions and their behaviour under weathering naturally varies in accordance with this fact.

In studying the behaviour of the two metasilicate groups we are at once confronted with a very curious fact, and one that is very difficult to explain on physico-chemical grounds, namely, the marked tendency of the pyroxenes to invert to amphiboles of an approximately corresponding composition. This is the phenomenon usually known as uralitization. It is nearly always to be observed in weathered specimens of gabbro or dolerite that the original augite is more or less converted to hornblende. It is often stated that this change is due to pressure (dynamic metamorphism), but this idea in reality only increases the difficulty, since hornblende has a larger specific volume than augite and in theory the inversion under pressure ought to take place in the opposite direction. In some instances there is evidence of a reaction between augite and iron ores (magnetite) giving rise to a hornblende richer in iron than the original augite, but this explanation does not go far. In very many cases, however, the secondary hornblende is very pale in colour in thin section and is best described as actinolite : it often shows also the fibrous or blade-like structure characteristic of the last-named mineral.

Summarizing the facts in the most general way possible, it may be said that the usual result of the weathering of the mixed ferromagnesian silicates is somewhat as follows : the magnesia molecule undergoes more or less hydration and may form some mineral of the talc or serpentine type ; if lime is present also, and the ground-water contains carbon dioxide, the result may be dolomite. If the original mineral contained a fair amount of alumina, some member of the chlorite group will be formed. Ferrous iron may also form a carbonate (siderite) or it may enter into the chlorite mineral to some extent, but the most common effect is more or less complete oxidation, usually to some form of brown hydrated ferric oxide, less commonly to hæmatite or magnetite. The lime molecule usually forms a carbonate, calcite or dolomite, or is often leached out altogether. In some cases it is found that the ferromagnesian silicates have been more or less completely converted into some member of the epidote group, though it is uncertain to what extent this process is to be considered as metamorphic. For this also a good deal of alumina is necessary and it appears that secondary epidote of this kind is often in part, or even wholly, derived from lime-felspar. It is probably to be regarded as due to a combination into one mineral of elements derived both from ferromagnesian minerals and from felspar.

Altogether our knowledge of the laws governing weathering in the metasilicates is in an unsatisfactory state, especially as regards the intermediate stages. The final result, however, may be summed up very briefly as consisting mainly in the separation of magnesia, mainly as carbonates and talcose minerals, of iron oxides and of calcium carbonate. Most of the silica is eventually carried away in the colloidal state.

A few words may be said about the alteration of the rhombic group of pyroxenes, since this subject is rather better understood. Enstatite, $MgSiO_3$ is usually converted into a form of serpentine, known as bastite, by the following reaction:

$$4(MgO.SiO_2)+CO_2+2H_2O=3MgO.2SiO_2.2H_2O+MgCO_3+2SiO_2$$

Here the change is assumed to be due to carbon dioxide, as a matter of convenience of expression, although it may be in reality simply a process of hydrolysis. The iron molecule separates as oxide or carbonate. The formation of bastite is essentially a process of serpentinization.

Olivine. The ordinary olivine of the basic and ultrabasic rocks is always an isomorphous mixture of the orthosilicates of magnesium and iron with sometimes a certain admixture of the corresponding lime silicate molecule. Hence its decomposition is in reality rather complicated, since these molecules yield different products. The iron silicate breaks up completely, yielding various oxides and hydroxides according to the degree of hydration possible in the circumstances. The first products of the oxidation may be either magnetite or hæmatite which stain the resulting rock black or red. The lime-molecule, if present, gives rise to calcite. The decomposition of the magnesian silicate is the most important part of the reaction, since this is usually the dominant component of the olivine. It may be most simply regarded as a process of hydrolysis, the product being the mineral known as serpentine, $3MgO.2SiO_2.2H_2O$. The reaction can then be represented by the following equation:

$$2Mg_2SiO_4 + 3H_2O = 3MgO.2SiO_2.2H_2O + Mg(OH)_2$$

Some writers prefer to attribute the decomposition to carbon dioxide dissolved in water; the equation then becomes:

$$2Mg_2SiO_4 + CO_2 + 2H_2O = 3MgO.2SiO_2.2H_2O + MgCO_3$$

This explanation is borne out in some cases by the presence of crystals of magnesite in serpentine rocks. Sometimes the serpentine undergoes a further and more complete dissociation, the final product being mainly magnesium carbonate. Deposits of magnesite formed in this way are now of considerable commercial importance as a source of material for basic furnace linings, magnesite being superior to dolomite for many purposes.

As a result of some recent investigations of the formation of serpentine in olivine rocks it is now suggested that at any rate some cases of serpentinization are to be regarded as pneumatolytic effects produced during the later stages of the cooling of the primary rock, and not as the effect of weathering. However this may be under deep-seated conditions, it is quite certain that the olivine crystals of some basalts, for example, are now undergoing a process of gradual conversion into serpentine at the ordinary temperature, as the result of superficial weathering processes.

The Accessory Minerals of the Igneous Rocks. Under this heading are included a considerable number of minerals occurring in igneous rocks, usually in very subordinate amount and of no significance in classification. Many of them are very stable and undergo little or no change as a result of weathering. Such are, for example, zircon, sphene, magnetite, rutile, garnet, corundum, monazite; apatite is common, but it is rather soft and fairly soluble in acids. Here also a brief mention may be made of a group of minerals common in acid rocks altered by pneumatolytic processes and in pegmatites, such as tourmaline, topaz, beryl, cassiterite and a vast number of other more or less rare substances. From these two categories are derived a large proportion of the hard and heavy constituents of sands and other sedimentary deposits. In basic igneous rocks ilmenite is very common and it weathers easily to a rather indefinite substance known as leucoxene, which appears to be a silicate of titanium allied to sphene. Here also are found in varying abundance members of the spinel group; picotite, chromite, etc. Not much is known about their decompositions. Platinum is also found in ultrabasic rocks. Nearly all igneous rocks contain more or less iron sulphide, as pyrites, marcasite or pyrrhotite, and these by their ready decomposition yield eventually iron oxides (usually hydrated) and sulphuric acid, the last-named being an important agent in further decompositions. It is not proposed to discuss here the numerous and complicated types of oxidation and weathering that take place in mineral veins, many of which are closely related to igneous rocks. This is a special subject of much importance, but an adequate description would occupy too much space, and a brief note would be useless. Only one very common phenomenon will be mentioned, namely the formation of a *gossan* or iron cap on the outcrop of sulphide veins. Nearly all mineral veins contain more or less iron pyrites and this on weathering forms with great readiness a deposit of hydrated ferric oxide (limonite) which is very insoluble and often forms a conspicuous red or brown cellular or slaggy mass along the outcrop of the vein, thus affording a valuable indication of the probable presence of ores below. The decomposition of copper pyrites produces a precisely similar effect, the copper being leached out as soluble copper sulphate leaving an iron cap on the surface. Gold being very insoluble often accumulates to a considerable extent in the gossan, if it is present in solid solution in the sulphides, as often happens: cassiterite also may behave in the same way, since it is very resistant to weathering.

The Weathering of the Igneous Rocks. From the foregoing examples it will be clear that the normal minerals of the igneous rocks are very susceptible to alteration by agencies that are in operation at surface temperatures and pressures. This means that under such conditions the minerals are in unstable equilibrium, a state of affairs which is perfectly natural when it is considered that these minerals are formed by crystallization from molten silicate melts in most cases at least at a red heat and many of them at temperatures comparable to those prevailing in a blast-furnace. The reason why these high-temperature minerals still continue to exist at and near the surface is because in them the adjustment to changed conditions takes place very slowly indeed: in some cases apparently almost at an infinitesimal rate, so long as they remain underground, protected from air and water and chemically active solutions. Near the surface mechanical agencies play a great part in paving the way for chemical changes, by favouring circulation of air and water in cracks and fissures, and in the pores of the rocks.

The general trend of weathering is in the direction of producing simpler compounds from more complex ones: oxidation, hydration and formation of carbonates are very prevalent, and under special conditions there may be formed sulphates, chlorides and analogous compounds essentially unknown in the unweathered rocks. All the processes that occur are of great complexity, owing to the large number of variable factors involved, and in many instances they are very incompletely understood. In particular we have as yet very little information as to the part played by colloidal systems in this field. Many of the ultimate products of weathering are undoubtedly of this nature: hence the difficulty of explaining many of the reactions by definite chemical formulæ, since it is necessary to take into account the phenomena generally summed up in the term adsorption, meaning the formation of compounds not in stoichiometric proportions. This subject is further discussed in Chapter XII. At any rate it is clear that the minerals of the igneous rocks give rise not only to definite new minerals, but also to silica-gels, colloidal aluminium and iron hydrates and many other similar substances, which in the present state of our knowledge render an exact treatment of the subject almost impossible. A further difficulty also arises in that in many cases the evidence is insufficient to distinguish clearly between the effects of true weathering under superficial conditions and various processes that are essentially of a pneumatolytic, hydrothermal or metasomatic character, such as the large-scale kaolinization and sericitization of alkali-felspar or the formation of certain types of serpentine. The persistence in many regions of slight relics of ancient volcanic activity in the form of hot and saline waters is responsible for a good deal of doubt as to the true nature of many superficial types of rock-alteration.

The Weathering of the Sedimentary Rocks. The fundamental principles of this part of the subject are entirely and essentially different from those just discussed. The sediments are laid down under superficial conditions, at the ordinary temperature and at atmospheric pressure and therefore consist of minerals that are stable under such conditions. Hence it would be unnatural to expect in them far-reaching changes in mineral constitution such as are found in the igneous rocks. But it has to be remembered that many of the sediments have undergone a good deal of change since their original formation, in the way of cementation and other forms of consolidation, loss of water by compression and so forth. And here we touch on a difficult subject, namely, the impossibility of deciding exactly what degree of alteration of a sediment by underground processes constitutes the lowest grade of metamorphism. This term cannot in fact be defined. However, it is agreed by most geologists that a well-cemented sandstone or a mudstone or even a moderately crystalline limestone still showing well-preserved fossils, shall not be considered to be metamorphic rocks. There is in the literature of geology a good deal of inconsistency in the terms applied to slates and quartzites, to quote only two examples out of many, and the application of the name marble is in a state of hopeless confusion, largely owing to its use by architects and the building trade for almost any stone that will take a polish, not necessarily even always a calcareous rock.

However, here an arbitrary division will be made and in this section will be considered the effects of weathering on such rocks as sandstones and grits in all their varieties, conglomerates, clays, shales and mudstones and all varieties of limestone and dolomite.

Generally speaking it may be said that the processes of weathering in the sedimentary rocks are mechanical and physical rather than chemical in their nature. Disintegration by the freezing of water and unequal expansion and contraction, or by alternate wetting and drying, play a very important part, as likewise does differential solution, especially by removal of cements differing in solubility from the clastic constituents of the rocks. Thus for example, a sandstone with a calcareous cement is very easily disintegrated by removal of the calcium carbonate by water containing carbon dioxide or other acids. On the other hand siliceous sandstones, and quartzites are much less easily broken up. Oxidation and hydration of ferruginous cements are important, especially among many of the older grey or green sandstones and greywackes, where the iron is largely in the ferrous state. The weathered crust on such rocks is always reddish or brown in colour. A well-cemented felspathic sandstone or arkose will weather in much the same way as a granite, yielding kaolin or mica as well as quartz. In all cases the quartz of the sediments is simply set free as such, and the "heavy minerals" also undergo little or no change, except that ilmenite is frequently changed to leucoxene. One of the characteristics of nearly all the loose superficial deposits is the presence of considerable amounts of iron oxides, usually hydrated ferric oxide.

Among the argillaceous rocks one of the most striking characteristics is the very common presence of great quantities of iron sulphide, sometimes as definite crystals of pyrite or marcasite, sometimes as very finely divided black ferrous sulphide, FeS: it is to this that the prevailing grey or bluish colour of so many clays, shales and slates is due, rather than to carbon, as commonly supposed. Some of the more distinctively black rocks of this group certainly contain a good deal of carbon, but even here ferrous sulphide is almost always abundant. The oxidation of this sulphide in weathering is one of the most potent causes of change in such sediments; on decomposition it yields, by a somewhat complicated reaction, hydrated iron oxide and sulphuric acid. The last-named is set free and in its turn produces further changes; by reaction with lime it often forms much gypsum. Since the texture of the argillaceous rocks is very fine there are great difficulties in determining both their original composition and the character of the secondary products yielded by them, and it is still a point of controversy as to what extent the clay-material of such rocks, both fresh and weathered, is in the colloidal condition. It is at any rate certain that most rocks of this kind, as well as soils, contain a large quantity of very finely divided micaceous material; this is no doubt partly derived from the comminution of primary mica and partly from the decomposition of felspars, as already explained under the heading of igneous rocks. However, much of the material of the finer clay rocks is beyond the resolving powers of the petrological microscope. The other principal constituents are minute grains of quartz and various carbonates, the latter often in an amorphous condition, at least so far as can be seen, though it is possible that even the minutest grains of calcite for example are really crystalline. The hydrated iron oxides, however, are certainly amorphous and perhaps exist as colloidal gels.

In short it may be said that the weathering of muddy rocks simply results in the re-formation of mud, but with its constituents commonly in a more oxidized and carbonated condition. Thus blue or grey clays yield brownish or yellowish soils.

The weathering of limestones, apart from mechanical disintegration, is in the main a question of solution, since calcium carbonate is readily soluble in water, especially in water containing carbon dioxide, which may be regarded as a dilute solution of carbonic acid. The reaction is as follows :

$$CaCO_3 + CO_2 + H_2O = CaH_2(CO_3)_2.$$

The calcium bicarbonate thus formed is, however, very unstable and is again easily dissociated, so that there is a strong tendency to deposition of calcium carbonate by springs issuing from a limestone rock, forming the various types of travertine and calc-sinter. It is unnecessary here to describe the physiographical features so characteristic of weathered limestones and the special characters of the underground circulation of water in calcareous rocks.

Most limestones, however, are more or less impure, the impurities being much less soluble than the limestone itself. This results in the very common occurrence in limestone regions of different types of residual superficial deposits, such as the Terra Rossa of the Mediterranean region and some of the curious clay soils found on the Chalk of southern England. Very many limestones are more or less ferruginous, the iron existing either as oxide or as carbonate (siderite). The last-named mineral is very unstable and is easily oxidized to ferric hydrate, or under specially dry conditions to the anhydrous oxide. Hence ferruginous limestones carry brown or red soils, as may be seen on many outcrops of the Jurassic limestones of the English Midlands. The Cornbrash is a very good example.

Many limestones, and especially those of the older rock series, are extremely impure, containing in addition to magnesia and iron a good deal of siliceous and aluminous material. These when weathered yield much clay substance of a muddy nature coloured brown or red by iron oxides. A remarkable feature in limestones of all kinds is the marked effect of differential weathering in developing the fossils that they contain: these are often invisible, or nearly so, on a fresh fractured surface, especially if the rock is somewhat crystalline, but on weathering they often stand out in high relief, being also frequently accentuated by colour-differences. Generally the reason for this behaviour is not clear: however, it can often be seen in microscope sections that the fossils are more coarsely crystalline than the matrix, and this may account for the difference of solubility, since large crystals are less soluble than small ones. In general the behaviour of dolomite rocks under weathering is essentially similar to that of limestones, though in some instances the porous and cellular structure of dolomites renders them even more easily attacked. In the case of the iron carbonate rocks the prevailing effect of weathering is oxidation and hydration rather than solution, the resulting iron oxides being very insoluble. This fact is of special importance in connection with the calcareous ironstones, such as those of the Lias. The iron-content of these when unweathered is often very low, and the amount of lime rather excessive, but the effect of atmospheric waters is to leach out the lime and thereby to concentrate the iron together with any silica that may be present, thus forming a siliceous brown oxidized stone at the outcrop of a calcareous bed, as in many places in Northamptonshire. This subject is a matter of very considerable practical and economic importance but cannot be discussed at length in this place.

The Weathering of the Metamorphic Rocks. It is hardly necessary to discuss at length the weathering processes in this group, since the minerals present are to a large extent the same as those of the igneous rocks. All the principal groups are there to be found, namely, quartz, the felspars, the micas, most of the pyroxenes and amphiboles, together with others such as garnet, the aluminium siliates, cordierite, staurolite and kyanite, specially characteristic of metamorphism. Many of the last-named are very stable and undergo little or no chemical alteration under ordinary conditions. In the calcareous varieties are found carbonates, especially calcite and dolomite, magnesia mica, forsterite, garnets and members of the epidote group. Very few of these minerals show characteristic reactions differing in any important respect from those that take place in the other great rock-groups, and the final products of weathering are in some sense intermediate between those of the igneous and the sedimentary rocks. A granitic gneiss naturally gives rise to products identical with those derived from a non-foliated granite, and similarly for other groups. A special characteristic of the residues from many metamorphic rocks is the great abundance of mica; and garnet, andalusite, kyanite, staurolite and rutile are set free in large quantities. Hence the superficial deposits in metamorphic areas are often very rich in "heavy minerals," as most of these are very stable as well as hard and heavy. Crystalline limestones (marbles) behave much the same on weathering as the less crystalline varieties. The prevailing schistose structure of the rocks of finer grain is on the whole favourable to mechanical disintegration.

Residual Deposits. It is a point of great importance in the geology of the sedimentary deposits that many of the gravels, sands, clays and other formations now forming the most superficial layers of the earth's crust are themselves strictly the results of the weathering in place of the underlying rocks. This is quite obvious in the case of soils, but it is sometimes not quite so obvious as concerns the subsoil ; nevertheless these residual weathered masses often extend down to very considerable depths, while owing to chemical changes and solution they often differ very widely indeed from their parent rocks. Thus residual clays may be formed from rocks of almost any kind by removal of the more soluble material with consequent concentration of the less soluble fraction. In nearly all rocks this least soluble part consists very largely of siliceous and aluminous material. If there is much free silica as quartz the residue will be of a sandy nature ; if it is mainly silicates of alumina of the type of kaolin or mica, as is very commonly the case, the residue will be essentially a clay. Such sands and clays, being in themselves in reality the products of weathering and therefore stable under the given set of conditions, do not readily undergo further changes, unless of course the climate or some other factor undergoes a marked variation. In general this question of the previous history of the material is of much importance in the study of soil-formation and serves to explain certain anomalous features in the characters of soils derived from apparently similar sources. The differences naturally depend largely on the degree of leaching that the material may have undergone at some earlier stage of its history. In any case it is essential to bear in mind that weathering may be a process carried on in several stages under varying conditions and therefore leading to complex results.

Complexity of Rock-Weathering. A comparison of lithological descriptions and chemical analyses of rocks, and especially of the sedimentary rocks, to be found in geological literature, will readily show the wide variations that are to be found in the composition of even the commoner rock-types and the consequent difficulty of drawing up any co-ordinated scheme or general rules governing their changes. In the following table are given a few selected analyses of rocks which by common consent would be regarded as coming under the various categories mentioned :

	A	B	C	D	E	F	G	H	I	J
SiO_2 .	96·87	97·58	80·88	90·30	45·22	60·15	·31	5·27	·22	8·50
Al_2O_3	1·34	·26	9·80	4·51	31·32	16·45	·64	1·07	1·37	6·12
Fe_2O_3	·44	·82	2·36	1·23	1·76	6·94	·69	1·03	·80	38·68
CaO .	·08	·05	·20	·15	·34	1·41	55·20	50·36	29·50	5·54
MgO .	·09	·19	·31	·23	·51	2·32	—	·56	21·02	3·75
K_2O .	·72	·12	1·13	·75	·94	3·60	—	·10	—	·03
Na_2O	·24	·14	·38	·12	·23	1·01	—	·20	—	·05
H_2O .	·25	·18	3·28	2·24	14·30	4·71	·20	·78	·27	4·05
CO_2 .	·04	·04	8·5	—	4·18	2·54	43·37	40·34	45·92	20·70

A. Quartzite, Hartshill, Warwickshire. Lower Cambrian.
B. Ganister, Lealholm, Yorkshire. Middle Jurassic.
C. Sandstone, Blackburn, Lancashire. Coal Measures.
D. Moulding Sand. Huttons Ambo, Yorkshire. Upper Jurassic.
E. Fireclay, Stourbridge, Staffs. Coal Measures.
F. Composite Analysis of 51 Palæozoic Shales.
G. Chalk, Newmarket.
H. Limestone, Silverdale, Kansas, U.S.A.
I. Magnesian Limestone, Sprotborough, Yorks. Permian.
J. Ironstone, Eston, Cleveland, Yorks. Middle Lias.

From the figures given above it is quite clear that such rocks must be composed of very varying mineral assemblages and therefore from the physico-chemical standpoint are to be regarded as highly complex and very variable systems, differing widely not only in the nature and proportions of the chemical compounds present, but also in the state of aggregation and stability of these compounds. Some of the high-grade glass sands and certain exceptionally pure limestones approach closely to simple systems of one and two components respectively, while some fire-clays for example are not very far from the silica-alumina system. The Chalk Marl of Cambridgeshire is an interesting example of a rock that can be regarded as a three-component system $CaO{-}Al_2O_3{-}SiO_2$: (see further, p. 144). But the great majority of rocks taken as a whole are really far too complex for detailed treatment on quantitative lines in the present state of our knowledge. The only possible way of elucidating their changes is by determination of the minerals present, followed by separate consideration of each, as has been done above in the case of the igneous rocks. Here again difficulties are introduced into the study of the sediments by the frequent presence of amorphous compounds and colloidal material with the attendant adsorption phenomena. On this subject as applied to rocks and their alterations our knowledge is still very inadequate.

The subject of rock-weathering in general has been carefully studied by Van Bemmelen from the chemical point of view.[1] He finds that the influence of climate is very notable: indeed he has been able to draw up a definite scheme of correlation between the type of climate and the general chemical character of the resulting products, as follows:

(1) In ordinary weathering in moist temperature climates the ratio of silica to alumina is approximately 3 : 1.

(2) In the kaolinitic type of decomposition the ratio is about 2 : 1. The climatic factor here is of uncertain nature.

(3) In the lateritic weathering of the tropics the whole of the silica is removed from the weathered product which consists mainly of hydrated oxides. Silica when present is found only in undecomposed minerals.

Whether a classification so precise as this can be maintained is at least doubtful, but in a general way it corresponds to the facts. The first group corresponds roughly to the residual clays and soils of the ordinary temperate cultivated districts: many other constituents are of course present, namely lime, magnesia, iron and alkalies, with the usual rarer constituents, phosphorus, sulphur, carbon, etc. A mixture of silica and alumina alone in the ratio of 3 : 1 would contain about 36 per cent. of alumina and 64 per cent. of silica by weight, and this is approximately the ratio that prevails in clays if all the other constituents are omitted and the alumina and silica recalculated to 100. In most cases, however, the ratio is modified by the presence of silica as sand-grains, which should be previously subtracted: hence in most analyses the amount of alumina comes out somewhat lower.

It is now generally agreed that kaolinization in the strict sense is to be attributed to some form of hydrothermal action, and it can therefore scarcely be looked on as a normal form of weathering, but impure kaolinitic clays, often called lithomarge, either white (pot-clay and pipe-clay), or stained various colours by oxides of iron and manganese, do result from what appears to be normal weathering under certain not well-defined conditions. The formation of laterite is discussed in some detail in the following section.

The Formation of Laterite. A brief reference has already been made to the decomposition of felspar to form hydrated oxides of aluminium (bauxite). This is only part of a large question, the peculiar type of weathering of silicate rocks in general that gives rise to the formation of the lateritic type of surface deposit, so characteristic of many of the warmer regions of the globe at the present day. Strictly speaking the formation of laterite is in reality a combination of weathering and deposition, but it is most conveniently treated here.

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[1] Van Bemmelen, *Zeits. für anorg. Chem.*, vol. xlii, 1904, p. 265, and vol. lxii, 1909, p. 221.

Laterite in the wide sense of the term is a superficial deposit, found over enormous areas in tropical and semi-tropical countries, especially in those with a monsoon type of climate and consequent strongly contrasted wet and dry seasons. This last point is believed to be of much significance with regard to its genesis. Taking the Indian laterites as an example, three types can be recognized, namely, ferruginous, aluminous or bauxitic, and manganiferous laterites. Some ferruginous laterites form quite high-grade iron ores, while others grade insensibly into bauxitic varieties. The lithological characters will not be described here, nor is it necessary to discuss the rather complicated nomenclature that has been introduced to describe the variations in composition.[1] The essential feature is that all the lateritic deposits consist of various hydrated oxides and hydrates, silica only being present in certain residual undecomposed minerals. This implies a very complete decomposition of the minerals of the original rocks. The origin of this type of decomposition is not known: it clearly depends on high temperature and it has been suggested by Holland that it may be due to bacteria.[2]

However this may be, the essential process seems to be as follows: Firstly, during the rainy season the primary minerals of the parent rocks are decomposed, the iron and alumina especially being converted into some soluble form, which is carried downwards by percolating ground-water: what becomes of the silica is not clear. Then in the dry season when surface evaporation is very active the solution is again brought to the surface by capillarity and the dissolved compounds on coming in contact with the air are oxidized and deposited in an insoluble form, usually as a cellular or slaggy mass of variegated colours. At first the laterite is quite soft, but rapidly hardens on exposure to air. These facts appear to indicate that the oxides are at first in a colloidal condition, as gels, and harden by loss of water. Felspathic acid igneous rocks give rise to the bauxitic varieties, while basic igneous rocks and ferruginous sediments yield the iron-ore laterites. The manganese laterite of India is formed from the manganiferous rocks (gondites and kodurites) that are the source of great supplies of manganese ores. Laterites and bauxites, formed doubtless in a similar way in past ages, are known in many of the older formations of continental facies, and form probably the best and most highly developed example of colloid chemistry in the geological sphere. The most obscure point in the whole subject is whether, and if so to what extent, bacteria may play a part in this process, as they undoubtedly do in other instances of iron-ore formation.

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[1] Fermor, *Geol. Mag.*, 1911, p. 514.

[2] Holland, *Geol. Mag.*, 1903, p. 59.

General Conclusions. From the foregoing very brief and imperfect sketch of the weathering processes in rocks certain general conclusions can be drawn. In the first place purely mechanical processes play a considerable part in the disintegration of all kinds of rocks. Secondly, solution is an agency of the first importance : its effects are, however, so intimately associated with processes of oxidation, hydration and hydrolysis that it is difficult to say how much is due to each : further the solvent is never pure water, but always contains acids, alkalies or salts, and purely chemical reactions of the type of double decompositions doubtless play a part. These may lead to precipitation as well as solution. The chemical equilibria concerned are nearly always of a complicated nature and generally cannot be expressed by simple equations. Since natural solutions are generally very dilute, dissociation of the dissolved compounds must be very complete. Furthermore it is certain that many of the processes and reactions concerned come within the sphere of colloid chemistry, a branch of the subject which has as yet been little applied to minerals and their decompositions.

With regard to the results of the processes, the general tendency is towards the production of simpler compounds from more complex ones. Compound silicates and aluminosilicates break up to simple silicates, often hydrated, or to oxides, hydrates and carbonates. The different molecules of isomorphous solid solutions often give rise to products of very different classes, and often much silica is set free, in the colloid form of dispersion. This is carried into the general ground-water circulation and is the origin of much of the silica cements of various sedimentary deposits at greater depths in the crust.

Further, it is obvious that the nature of the processes that go on, and the final results of these processes, are to a very great degree controlled by climate : this is merely another way of stating the obvious truth that temperature and presence or absence of water are factors of the highest importance and really controlled the workings of the other agencies. Since weathering is a purely superficial process it may be assumed that atmospheric pressure alone is concerned, at any rate from the chemical point of view.[1] Another subject, still highly obscure and hardly touched on here, is the possible influence of bacterial action on weathering. As to this there is little positive information and in any case the changes due to this cause are in ultimate analysis chemical or physical in their nature, and it is not of much importance whether a given and determinable result is produced by an organic or an inorganic agency.

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[1] For a discussion of the effects of pressures due to freezing of water in closed spaces in rocks see p. 16.

CHAPTER IX

THE SALT DEPOSITS

The geology of the salt deposits has been the subject of a large amount of investigation, mainly on account of its technical and industrial importance. The subject has also been worked out very thoroughly on the physico-chemical side, and it may perhaps be said with truth that no other branch of geology rests on so sure a basis of theory and experiment. It will be necessary in later pages to quote freely from the epoch-making work of van't Hoff and his colleagues, but as a preliminary some attention must be paid to the more general relations involved.

It is hardly necessary to attempt a definition of salt deposits. The underlying idea is the very simple one that the minerals concerned are more or less readily soluble in water at the ordinary temperature and pressure, and that their separation in the solid form is due to special and distinctive geological conditions, which depend very largely on physiogra~~phy and climate~~. For details on these points reference must be made, if necessary, to some textbook of physical geology. In what follows acquaintance with these fundamental principles will be assumed.

Solubility. It is probable that all minerals are to some extent soluble in water, even at the ordinary temperature, but in a very large number of instances the solubility is so small as to be inappreciable. This is the case for example with nearly all the natural silicates, and with most of the sulphides, oxides and hydroxides. As a matter of fact, nearly all the metals possess some soluble compounds, as shown by the usual methods of chemical analysis, but to put the matter into a generalized form, it may perhaps be said that the principal substances of geological importance that are freely soluble are the chlorides, sulphates and nitrates of the alkali metals and magnesium, the carbonates of potassium and sodium, some of the salts of calcium and several compounds of iron. Such salts as the carbonates of the alkaline earths and calcium sulphate occupy a somewhat intermediate position, being quite appreciably soluble, though not readily so. Many other examples of more or less soluble mineral substances may be quoted, but enough has been said to give a general idea of the class of compounds involved: details will appear later.

As is only natural the solubility of these salts varies very widely indeed; in general terms, and this is an important point, the most soluble salts are those of potassium and magnesium, followed by sodium. Another factor of considerable geological significance is the rate of change of solubility with rise or fall of temperature, much variety existing in this respect. In dealing with the crystallization of salts from natural solutions it is also necessary to take into account the very important principle that the solubility of a given salt in a mixed solution is controlled by the nature and amount of all the other salts present in the solution, so that the relations and order of crystallization often become very complex: furthermore, as temperature and pressure are varied the equilibrium conditions in the solution are altered, changes taking place in the constitution of the solid phase in contact with the solution. This has a special bearing on the formation and decomposition of double salts, a common phenomenon and a matter of considerable technical importance, especially in the purification of natural salts. Altogether the physical chemistry of the salt deposits is a matter of extreme complexity, and only the most general sketch can be given here.

Sea-Water. The first example of a natural salt solution that suggests itself to everybody is the water of the sea. Even if only the more abundant constituents are considered, this is a fairly complex solution. In analysis of a mixed salt solution the percentages of the basic and acid radicles are of course determined separately and it is very much a matter of personal choice how they are grouped into salts. Since such solutions are for the most part dissociated and ionized, it is evidently purely an arbitrary arrangement in any case. The following figures, taken from the *Challenger* Report, are generally accepted as giving the salt-content of the waters of the open ocean, from the average of many samples collected far from land: 1,000 parts of water contain about 34·4 parts by weight of soluble salts and the percentage composition of this dissolved matter is shown in the following table:

Sodium chloride	77·758
Magnesium chloride	10·878
Magnesium sulphate	4·737
Calcium sulphate	3·600
Potassium sulphate	2·465
Magnesium bromide	·217
Calcium carbonate	·345
	100·000

However, although the composition of the salt appears to be very constant the total salt-percentage of sea-water varies widely under different conditions, especially in partly enclosed seas, where there may be a great or small inflow of fresh water from rivers, and a varying degree of evaporation, according to temperature. Thus some seas, such as the Mediterranean, may be salter than the open ocean, while others, such as the Baltic, contain much less salt. In such seas also there are naturally local variations ; for example, just off the mouth of a large river, or in a small or nearly enclosed coastal bay or lagoon in a hot climate.

The first general conclusion to be drawn is that the water of the open sea is very far from being a saturated solution for any of the common soluble salts, and deposition of such on any important scale from sea-water can only take place under very special conditions, such as only rarely occur in nature. What these conditions may be will be considered later, after the phenomena shown by terrestrial salt deposits have been studied.

The Waters of the Land. A distinction is commonly drawn both in scientific and in popular writings between *salt* and *fresh* water : in point of fact the distinction is only one of degree, as there is no such thing in nature as perfectly pure water. All terrestrial waters contain more or less dissolved material ; often a very considerable, though highly variable amount, as witness the common references to hard and soft water, chalybeate springs, saline springs and so forth, and many terrestrial salt lakes are very much salter than the sea. It will perhaps be instructive to place side by side the figures showing the content of a few important salts in normal sea-water and in some well-known salt lakes.

SALT CONTENT OF SEA WATER AND SALT LAKES

in parts per 1000.

	Sea Water.	Dead Sea.	Great Salt Lake, Utah.	Lake Elton.	Lake Urmiah, Persia.
Sodium chloride .	26·73	63·86	118·63	38·3	190·47
Magnesium chloride	3·75	163·67	14·91	197·5	5·22
Magnesium sulphate	1·63	—	—	53·2	8·00
Calcium sulphate .	1·24	·78	·86	—	1·81

The differences are therefore seen to be enormous, especially in the proportions of sodium and magnesium salts : only calcium sulphate is fairly constant all through. There are also lakes, such as those in western Egypt and Carson Lake, Nevada, specially characterized by abundance of sodium carbonate, which may be called natron or alkali lakes. It is evident then that such lakes have not been formed merely by isolation and concentration of sea-water in tectonic basins. Some other factor has certainly come into play.

It is a conspicuous fact that salt lakes are only found in arid regions, and of course they never possess a permanent outlet. To cut short the geological discussion it may be said that salt lakes are only formed in regions of inward or centripetal drainage, where the annual evaporation is greater than or equal to the rainfall. Since there can rarely be exact equilibrium it follows that such lakes are usually drying up. No case seems to be known where a salt lake is increasing in size.[1]

In a somewhat different category are the waters of the Aral-Caspian basin, for example. The Caspian and the Sea of Aral being now entirely without communication with the sea, are strictly speaking salt lakes, but geological evidence shows that at a comparatively recent date such communication did exist, and they must be regarded as masses of original sea-water which has been modified since the separation: as a matter of fact the salinity of the Caspian shows much local variation, being low at the northern end, owing to the inflow of the Volga and other great rivers, and much higher at the southern end, which lies well in the arid climatic belt.

An enormous number of analyses of terrestrial waters of all kinds have been published, but so much local variation is shown that no good purpose is served by an attempt to draw up any generalizations on the subject. Not only does the salt-content of river waters vary widely according to the kind of rocks undergoing decomposition within their catchment basin, but in many cases the composition is profoundly affected by the presence of saline springs or beds of soluble salts. Much of the salt in the waters of the Dead Sea, for example, is now believed to be derived from salt beds of ancient date in the valley of the Jordan, while as is well known the waters of limestone regions are always very *hard*, owing to the presence of dissolved calcium carbonate.

The Primary Source of Soluble Salts. The ultimate source of soluble salts, like all other purely terrestrial matter, is to be found in the decomposition of the minerals of the primitive solid crust, which is the same thing as saying that they are formed by decomposition of igneous rocks. As before stated the salts of sodium, potassium, and magnesium are the most abundant and the most soluble, while calcium salts, though usually less soluble,[1] are of great geological importance.

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[1] There is a possibility that Tanganika was more salt fifty years ago than it is now, but the evidence is inconclusive.

The bases of these salts, potassium, sodium, magnesium and calcium, are present in abundance in the primary igneous rocks as felspars (and felspathoids), micas, amphiboles, pyroxenes and olivine. Of the acid-forming elements, sulphur occurs commonly in igneous rocks in the form of sulphides, while chlorine is undoubtedly present in some quantity, though not very much is known of its occurrence in igneous rocks. According to F. W. Clarke [2] the average percentages of sulphur and chlorine in all igneous rocks are 0·100 and 0·064 respectively. In some pneumatolytic modifications of igneous rocks chlorine is considerably concentrated (e.g. in chlorapatite and in scapolite rocks), while the abundance of sulphides in many ore deposits scarcely needs emphasis. It is also clear that much sulphur and chlorine are emitted by volcanoes, thus adding to the stock at the surface. There is thus no difficulty in accounting for the presence of soluble salts in considerable quantities in natural waters: most of these quickly find their way to the sea, and for the most part remain there, so that the sea must be continually becoming more salt, but nevertheless there may be occasionally an important system of what may be called circulation of salts; this may happen if an arm of the sea (like the Caspian) is cut off and evaporated to dryness, the salt beds thus formed being buried in sedimentary strata and afterwards exposed by denudation and dissolved by meteoric waters. But on the whole when soluble salts reach the sea they stay there, and on this basis attempts have been made to calculate the age of the earth, or rather of the oceans, the data being the volume of the oceans, their salt content and the total amount of salts carried down annually by all the rivers of the world.[3] The last-named figure obviously leaves a very wide margin of error.

The solution and transport of calcium carbonate in natural waters, and especially its final destination, is a somewhat more complicated matter: two important and totally distinct factors are here concerned. In the first place the solubility of calcium carbonate depends very largely on the amount of carbon dioxide dissolved in the water, since calcium carbonate and carbon dioxide react to form a so-called bicarbonate, which is much more soluble,

$$CaCO_3 + H_2CO_3 \rightleftharpoons CaH_2(CO_3)_2$$

but this dissociates easily on slight rise of temperature and the simple carbonate is deposited; further, pressure has a very important influence on the stability of the bicarbonate. When water rich in bicarbonate rises from a great depth, as in some hot springs, on release of pressure at the surface dissociation occurs and the carbonate is deposited, usually as aragonite.

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[1] Calcium chloride and nitrate are very soluble, but calcium sulphate is not, thus forming a strong contrast to magnesium sulphate.

[2] *op. cit.*, on p. 91.

[3] See Joly, *Trans. Royal Dublin Soc.*, 1899.

Secondly, although vast quantities of calcium carbonate reach the sea, the water contains a very small percentage, most of it being snapped up by calcareous organisms to form shells and other structures.

During the course of geological history, since the formation of the primitive crust and the beginning of sedimentation, there has been a continuous addition to the total stock of soluble matter in circulation at and near the surface, and this stock naturally tends to concentrate in the hydrosphere. On occasion isolated portions of the hydrosphere may dry up by evaporation and salt-deposits are formed. Also in many arid parts of the world a good deal of salt is deposited by efflorescence, either actually on the surface or in the upper layers of the crust, as in the salt deserts of south-western Asia. Salt-pans are by no means uncommon in South Africa, for example: many of them are dry for part of the year, and contain brine in the rainy season.

Salt Deposits of Ancient Date. Beds of rock-salt and gypsum, less commonly of anhydrite, are found at many horizons in the sedimentary series. This is not the place to discuss in detail the geology of these occurrences. Particulars will be found in physical and stratigraphical textbooks. It will here suffice to say that many of them, probably the majority, have been formed by the desiccation of inland lakes, but in some cases the enormous thickness of such deposits, amounting to several thousand feet, can only be explained by the evaporation under special conditions of vast volumes of sea-water in a nearly enclosed marine basin, the conditions being such that there was a continuous inflow of water to supply the loss by evaporation. Such seems to have been the case with the Stassfurt salt-deposits, the most important in the world and the best known. It appears that in some instances there has been a good deal of underground movement of such salts after their first deposition. They have been dissolved in areas of compression and redeposited in such places as the cores of anticlines, and as domes at the crossing of two folds, thus accounting for some exceptional thicknesses.

Although, as above stated, rock-salt and gypsum beds are very common, this is by no means the case with salts of potassium and magnesium. Owing to the very high solubility of these, they are not deposited unless desiccation is complete, or very nearly so, and this seems rarely to have happened. Only three definite cases are known: at Stassfurt in central Germany; in Alsace; and in N.E. Spain. At Stassfurt some barrier must have arisen to put an end to the inflow of sea-water, so that the whole finally dried up. The conditions in the other areas are not so well known.

Experimental Work on Sea-Water. Special interest attaches to the products of the evaporation of sea-water, mainly owing to the bearing of this subject on the study of the Stassfurt salt deposits. As early as 1849 Usiglio carried out experimental work, but his results were unsatisfactory, since he began with natural sea-water, which is a highly complex solution, and also he did not succeed in avoiding supersaturation. Later the problem was attacked from the other end by van't Hoff, who started with the more simple systems, and gradually worked up to the more complex ones, representing his results largely by space models. Owing to the number of components that have to be taken into account and the common occurrence of double salts and varying degrees of hydration, the subject is extraordinarily complicated, and only a very few of the simpler cases can here be considered.[1]

Gypsum and Anhydrite. When sea-water is concentrated by evaporation the first salt to crystallize is calcium sulphate, and this fact accounts for the abundance of this substance in nature. Calcium sulphate is found in nature in two forms, as gypsum, $CaSO_4.2H_2O$, and anhydrite, $CaSO_4$. The physical relations between these forms have been worked out in detail and are of considerable interest. The behaviour of calcium sulphate in solution is somewhat peculiar: it is commonly stated that its solubility decreases on rise of temperature, but this does not appear to be strictly true.[2] Up to about 40° the solubility, according to the latest results, appears to increase slightly, and then begins to fall off. There is no break in the curve at the maximum, so far as has been ascertained, though this statement is open to suspicion. At about 63·5°, however, there is a decided break in the curve, the solid phase in contact with the solution changes to anhydrite, and the solubility thereafter falls very sharply. From the geological point of view, however, the most important fact is that the presence of other salts in the solution has a very marked effect on the position of the gypsum-anhydrite inversion-point, so that on evaporation of sea-water or of salt lakes anhydrite can form at much lower temperatures. Thus in a saturated solution of sodium chloride gypsum is unstable above 36°.

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[1] For details, see van't Hoff, J. H., *Zur Bildung der ozeanischen Salzablagerungen.* Brunswick, 1909, and *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen.* Leipzig, 1912. For a summary in English see Armstrong, H. E., *Rep. Brit. Ass.*, Glasgow, 1901.

[2] Many of the earlier figures appear to be incorrect, owing to the occurrence of supersaturation, which readily takes place in such solutions.

From the geological standpoint it is hardly necessary to deal with the well-known partial dehydration of gypsum to the hemihydrate (Plaster of Paris), since in air the transition temperature is about 100°; in a salt-solution about 76°; and in pure water about 66°, so the change does not occur in nature. Also the fact that all the forms, gypsum, hemihydrate and anhydrite are dimorphous has no geological application, though of interest to mineralogists.

Fig. 57 shows the solubility-relations of gypsum and the two forms of anhydrite; the curve for the unstable form of the latter is inserted only because it is useful in fixing a point on the unstable continuation of the gypsum curve.[1]

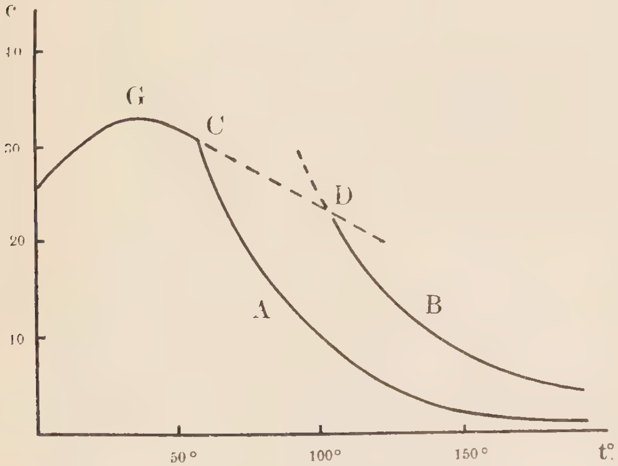

Fig. 57.—The solubility of calcium sulphate.

GC = solubility curve for gypsum; *CA* for natural anhydrite; *DB* for "soluble anhydrite."

Solubility of Salt Mixtures. As an illustration of the solubility relations of salts in mixed solutions we may take the particularly simple case of the chlorides of potassium and sodium, which is not complicated by the formation of double salts, while within the ordinary temperature range no solid hydrates can exist, though in some salt lakes in Siberia a hydrate, $NaCl.2H_2O$, has been found below 0° C.

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[1] Hulett and Allen, *Jour. Amer. Chem. Soc.*, vol. xxiv, 1902, p. 667.

At 20° the solubility of these salts in simple solution is nearly equal, namely 25·6 per cent. for KCl and 26·4 per cent. for NaCl, but the addition of NaCl to a saturated solution of KCl has a great effect in lowering the solubility of the latter, while the solubility of NaCl is also lowered in a less degree. The solution saturated for both salts at 20° contains only 10·2 per cent. KCl and 20·3 per cent. NaCl. These relations are conveniently shown in Fig. 34 which in reality represents an isothermal section of a solid model. Fig. 58 shows in a similar way the change in the composition of the solution saturated for both salts: each pair of co-ordinates gives the percentage of each salt in the solution at the corresponding temperature, while the heavy line shows the change. It is to be noted that there is a considerable analogy between the point *C* in Fig. 34, and the heavy line in Fig. 58, on the one hand, and eutectic points and eutectic boundary curves on the other hand. The particular case under discussion has a technical application of some importance in the preparation of pure potassium chloride from the mineral sylvinite, which is a mixture (or solid solution) of KCl and NaCl. It is evident that by adding more NaCl solution to a saturated solution at a high temperature KCl can be precipi-

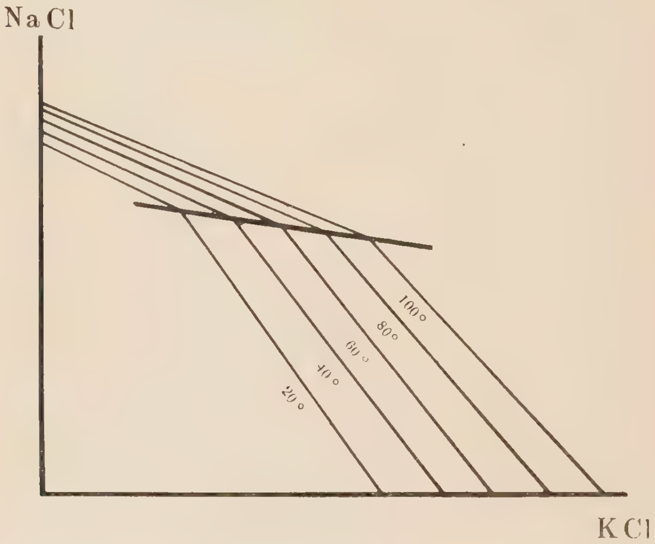

FIG. 58.—The solubilities of mixtures of NaCl and KCl at different temperatures.

The thick line shows the composition of the solutions saturated for both salts.

tated, since its solubility decreases on cooling while that of NaCl increases.

This type of solubility curve for a system of two solid phases is called incongruent, since the solubilities of each vary in opposite directions, and the curve is directed towards both the concentration axes.

If the solubility of *both* salts in the saturated solution increases with rise of temperature the curve will run the other way, and a continuation would cut one axis only. This would also be the case if both solubilities were less at the higher temperature; from a congruent salt-pair neither salt can be obtained pure by cooling a doubly saturated solution.

The Chlorides of Potassium and Magnesium. One of the most important systems studied by van't Hoff and his colleagues in their investigation of the Stassfurt salt deposits is that comprising the chlorides of potassium and magnesium. The natural deposits of this group are of very great technical importance as sources of potassium compounds, but the whole thing is extremely complicated. As the subject is treated very fully in many textbooks of physical chemistry only the briefest mention of it will be made here. It so happens that these salts can combine to form a double salt, carnallite, $KCl.MgCl_2.6H_2O$, and there are also several possible hydrates of $MgCl_2$. The one that occurs in the natural salt deposits is bischofite, $MgCl_2.6H_2O$. Hence the possible salts that can occur are sylvite (KCl), carnallite and bischofite. But the behaviour of carnallite is peculiar: as a solid phase in contact with a solution it is only stable in presence of an excess of $MgCl_2$; a pure saturated solution of carnallite cannot exist; and at all temperatures carnallite is decomposed by water, with separation of KCl. Further, at a high temperature (about 168° C.) dry carnallite melts, with separation of the same KCl. Natural salt deposits always contain rock salt in addition to potassium and magnesium compounds: when these mixed salts are treated with water the presence of NaCl alters the solubilities of the other salts and thus introduces further complications. On all these facts there have been founded a variety of industrial processes for recovery of potash, but the details of these are outside the scope of this book.

Mixed Chloride-Sulphate Solutions. Owing to the abundance of sulphates as well as chlorides in many salt deposits it becomes necessary to study the behaviour of solutions containing two acid radicles. For this purpose we may select the system $K–Mg–SO_4–Cl$.

In a system of this kind, disregarding for a moment the possibility of double salts, the equilibrium can be expressed by an equation of the form

$$AB + CD \rightleftharpoons AC + BD.$$

Here the possible products are KCl, $MgCl_2$, K_2SO_4, $MgSO_4$, and the equation becomes

$$2KCl + MgSO_4 \rightleftharpoons K_2SO_4 + MgCl_2.$$

According to the phase rule it then becomes necessary to consider how many components are present. At first sight there appear to be four, but this is not so in reality. The number of components is defined as the least number of separate substances by which the reactions can be expressed, but since negative signs are ruled to be admissible, any one of the four salts, K, L, M, N connected by such an equation can be expressed in terms of the other three, thus,

$$\begin{aligned} \text{if } K + L &= M + N \\ \text{then } L &= M + N - K. \end{aligned}$$

Hence in a solution of this kind there are three components in addition to the water, and the system becomes quaternary. The four possible salts connected by a relation of this kind are called reciprocal salt-pairs. Unfortunately, however, even this commonly occurring case is complicated by the existence of many double salts, as well as varying degrees of hydration of the salts, so that the diagrammatic representation becomes very complicated, and cannot be given here. Since at Stassfurt NaCl is also always present, the confusion becomes worse.

The behaviour of the whole system has been studied by van't Hoff at all temperatures between 25° and 83°. He finds that the order of separation of the salts falls into three main periods, each characterized by a particular salt, in addition to others having a much wider temperature-range, thus :

First period, from 25° to 37° :

crystallization of schoenite $K_2SO_4.MgSO_4.6H_2O$. at	26°
reichardtite $MgSO_4.7H_2O$	31°
$MgSO_4.6H_2O$	35·5°

Second period, from 37° to 55° :

langbeinite $K_2SO_4.2MgSO_4$	37°
loeweite $Na_2SO_4.MgSO_4.2\frac{1}{2}H_2O$	43°
vanthoffite $MgSO_4.3Na_2SO_4$	46°

Third period from 55° to 83° :

astrakanite $Na_2SO_4.MgSO_4.4H_2O$	60°
leonite $(K,Na)_2SO_4.MgSO_4.4H_2O$	61·5°
kainite $KCl.MgSO_4.3H_2O$	83°

A comparison of these experimental facts with the salts actually found at Stassfurt has yielded some very interesting and rather unexpected results. It is found that many of the salts characteristic of the higher temperature ranges do actually occur there, and it has to be concluded either that these salt-deposits were formed at incredibly high temperatures, or that they have undergone a considerable degree of metamorphism since their formation. This alteration is believed to have been due to heated waters circulating during periods of mountain-building, although the deposits are now absolutely dry in depth.

As an example of the kind of alteration thus effected, the type of salt-deposit rich in carnallite may be selected (carnallite-rock). If this is treated with water at 72°, much more $MgCl_2$ is extracted than any of the other constituents, and the result is a mass of sylvine, kieserite and rock-salt (the so-called Hartsalz), while at lower temperatures a similar leaching leads to formation of kainite and rock-salt. Both of these types of salt-rock are found at Stassfurt, and kainite is of considerable importance as an " artificial " potash-manure, whereas sylvine and carnallite are better adapted as sources of potash for the processes of industrial chemistry, since they contain only the chloride radicle.

Alkaline Carbonate or Natron Lakes. These lakes form a special class of limited distribution but of considerable interest. In them sodium and potassium carbonates and bicarbonates are deposited, with chlorides and sulphates in varying proportions. The examples best known to European geologists are the natron lakes of Egypt, but similar types are known in Hungary, Armenia, Venezuela, Nevada and Southern California.[1] Those of the western United States have been more completely investigated than any of the others, and here the lakes are often associated with large areas of alkaline soils, rendered barren or nearly so by the large amount of salts formed at and near the surface as an efflorescence due to ascending waters.[2]

Alkali salts of this type appear to be always formed under arid climates and under very special conditions: the exact chemical reactions that go on, and indeed the general source of the peculiar salts present, are not yet understood.

In most instances, judging by published analyses, the dominant salts are sodium carbonate and sodium sulphate, with a smaller proportion of sodium bicarbonate: sodium chloride is commonly quite subordinate, while some examples contain a considerable amount of sodium nitrate. Potassium salts are also present and in some cases, though rarely, in considerable amount. Two analyses of solid incrustations from California showed 20 and 26 per cent. of potassium sulphate, though this is exceptional. Sometimes borates are also found: this type is described in a separate section. (See p. 188.)

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[1] Clarke, F. W., *The Data of Geochemistry*, *Bull.* 770, U.S.G.S., p. 237.

[2] In America the term alkaline is used in a wider sense than in Europe, to indicate almost all kinds of salts in lakes and in soils; " white alkali " there means chlorides and sulphates (saline lakes and soils of most European writers), while the carbonate salts are generally called " black alkali " since the soils permeated by them are often of a very dark colour.

An analysis of the water of Owens Lake, California, showed the presence of 77 grams per litre of dissolved salts, which included approximately 35 per cent. Na_2CO_3, 7 per cent. $NaHCO_3$, 14 per cent. Na_2SO_4, 38 per cent. NaCl, and 4 per cent. KCl. (The figures are rounded off to the nearest whole number.) From this lake "natural soda" is prepared on a commercial scale.[1] The soda-lakes of Ragtown, Nevada, are also extremely rich in carbonates and bicarbonates, with very little chloride.[2] These must serve as examples of a common type.[3] Some of these lakes, locally called *Playas*, are dry in summer and flooded to the depth of a few inches in the wet season. In this they resemble the *pans* of South Africa,

The natural mineral forms assumed by the above salts on crystallizing are rather remarkable: they include natron, $Na_2CO_3.10H_2O$ (identical with common washing soda); trona, $Na_2CO_3.NaHCO_3.2H_2O$, and thermonatrite $Na_2CO_3.H_2O$. Of these trona is the commonest. The Ragtown soda lakes also deposit gaylussite, $CaCO_3.Na_2CO_3.5H_2O$, although the analyses of the waters show no lime. The minute quantities of calcium brought in by streams are probably precipitated immediately.

The Soda Lakes of Egypt. The long-famous natron lakes of Egypt lie in the desert region some 25 miles N.W. of Cairo in the Wadi Natrûn, at about 30 to 50 feet below the level of the Mediterranean; the lakes which are about a dozen in number form a chain about 15 miles long, running in a N.W. direction. The waters contain abundance of sodium carbonate, sulphate and chloride, and the salts in solid crystalline form also lie on the floor of the lakes in thick masses, showing several different types. The natron may be either in solid masses, or as an aggregate of needle-like crystals. Incrustations of salts are also found on the sands around the shores. The chemical composition of the "soda" as shown by analysis corresponds nearly to the formula for trona, given above. Numerous small streams running into the lakes contain the same salts in solution, and as the evaporation appears to equal the inflow the lakes are gradually becoming more concentrated. However, the primary source of the salts has not been explained. Several frankly speculative theories have been put forward, but there is so little evidence that they need hardly be set out here. The most probable explanation is that water from the Nile, with dissolved calcium bicarbonate, percolates into the valley through strata rich in sodium chloride and calcium sulphate, and the sodium salts are formed from the calcium salts by double decomposition.[1]

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[1] Chatard, *Bull.* 60, U.S.G.S. 1890.

[2] *Ibid*, p. 52.

[3] Numerous analyses of such waters will be found in Clarke, *Data of Geochemistry*, 5th edition, *Bull.* 770, U.S.G.S. 1924, with full references to the literature.

Potash Salts. It has already been pointed out that owing to their high solubility salts of potassium (and magnesium) can only be deposited when salt lakes have been completely dried up, or very nearly so. For some reason or other this has very rarely happened, and but few instances of such deposits are known. The most famous of all are the Stassfurt salts, which were an important factor in the commercial and agricultural development of the German Empire. For an account of the physical chemistry of these deposits see page 183. Somewhat similar occurrences are also known in Alsace and in N.E. Spain, but details need not here be given since no new principles appear to be involved.[2]

There is, however, an extraordinary deposit of potash salts in Abyssinia which presents some very remarkable features. This area, which lies on both sides of the frontier between Abyssinia and the Italian colony of Eritrea, evidently formed part of the Red Sea, which has been cut off by uplift of a barrier and volcanic accumulations. It extends to nearly 400 feet below sea-level and is one of the hottest places in the world, the average shade-temperature being over 120° F. It is probable, however, that the drying up of an arm of the sea is not the whole story, since the salts are of very peculiar composition. In the centre of the sunken area, known as the Piano del Sale, rises Mt. Dellol, a mountain of rock salt, which just reaches sea-level. At the S.E. corner of this hill is an area of some 40 acres covered by a layer of sylvite, KCl, from 2 to 5 feet thick. Around this lie some 400 acres of carnallite, which is at least 150 feet thick, and bore-holes show that this probably has a plug-like form, with steep boundaries. Then comes rock salt covering the plain for many miles, and the outer margin is a broad belt of gypsum. The salt and gypsum beds dip towards the centre of the basin.

Here, then, we have a basin occupied by the normal succession of salts, as deposited from sea-water ; gypsum, rock-salt, potash salts ; indicating the drying up of an arm of the sea in a land-locked basin. But a series of hot springs varying from 50° to 90° C., saturated with $MgCl_2$, rise through the carnallite zone, and there are thick beds of sulphur N.E. of Dellol. There is abundant evidence of volcanic activity in the neighbourhood, and there is a strong suggestion that some of the salts are of volcanic origin.

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[1] Schweinfurth and Lewin, *Zeits. Gesell. f. Erdkunde*, vol. xxxiii, 1898, p. 1.

[2] For particulars, see *Potash*, by S. J. Johnstone, Monograph Imperial Institute, 1922, pp. 11 and 15, with references to the literature.

Owing to the intense heat of the climate the separation of potassium chloride in commercial form is very easy, since carnallite exposed to the sun here melts in its own water of crystallization, depositing solid KCl, while the solution is drained away. This solution is saturated for carnallite, which is deposited on further evaporation, and again breaks down as before : thus by a continuous repetition of the process a product containing 80 per cent. KCl is finally obtained for transport to the coast.[1]

Boron Compounds. In several parts of the world salts of boric acid are found in considerable quantity under somewhat peculiar conditions. The occurrences vary a good deal in geological character, and it seems probable that they are due to different sets of causes. In general terms there is evidence that some of the deposits are of direct volcanic origin, while others come within the category of salt deposits as defined in this chapter. As a matter of convenience only, all will be here treated together.

The three principal regions in which boron compounds occur in commercial quantity are Italy, California and Tibet. As to the last-named, which has long been an important source, very little is known, but what evidence there is suggests that the crude borax, known as *tincal*, is found in salt lakes on the high plateau. The conditions are probably very similar to those obtaining in California, and need not be further discussed.

The occurrences of boric acid in Italy are quite clearly of volcanic origin. The so-called fumaroles or soffioni of Tuscany are jets of steam emerging from the ground carrying large quantities of boron compounds as vapours. The steam is made to pass into water in tanks and the resulting solution is then concentrated by the natural heat of the steam jets, depositing boric acid, H_3BO_3. and ammonia salts : a little H_2S is also present.

Most natural salt-deposits contain more or less boron, and the curious mineral boracite is found at Stassfurt, for example. But the usual compounds are borax, colemanite and ulexite. All of these are abundant in certain parts of the arid regions of the western United States and the occurrences have been carefully investigated. It is to be noted that this area not only shows pronouncedly arid conditions, favourable to salt formation, but is also a region of recent volcanic activity. The boric salts have obviously been concentrated in lakes without outlet, in the usual way, while the primary source of the boron is to be sought in volcanic emanations. It is hardly necessary to enter into a detailed discussion of the mineralogical character and sequence of the deposits.

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[1] Guia, *Atti R. Acad. Lincei*, vol. xxvii, 1918, p. 331. Holmes, *Geol. Mag.*, vol. lvi, 1919, p. 340. Bibolini, *Comptes Rendus xiii Congr. Géol. Internat.* Brussels, 1922, p. 805.

Formation of Calcium Carbonate Deposits from Solution. An account of the geology of natural deposits of calcium carbonate from the waters of springs and streams, in caves and elsewhere, will be found in any textbook. Here it is only necessary to discuss very briefly the physico-chemical side of the subject.

The solubility of calcium carbonate in pure water is rather low, though considerably higher than that of most silicates, for example. Nevertheless, nearly all natural waters contain more or less of this compound, while in some the amount is large enough to impart to the water properties that from many points of view are undesirable, known collectively as " hardness." It must be noted that in many instances the hardness is due to the presence of dissolved calcium sulphate, rather than the carbonate, and this form of hardness cannot be removed by boiling.

When water contains dissolved carbon dioxide its content of calcium carbonate may be greatly increased, since $CaCO_3$ and CO_2 react in solution to form a calcium bicarbonate, which is much more soluble :

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons CaH_2(CO_3)_2$$

This is a reversible reaction and the equilibrium condition is determined by the gas pressure. In practice this means that when the water is underground, under pressure higher than that of the atmosphere, the calcium is kept in solution as bicarbonate, but when the water issues as a spring or drips from the roof of a cavern, the equilibrium shifts to the left-hand side of the equation and solid $CaCO_3$ is deposited as stalactites, travertine or calc-sinter, which consist of crystalline calcite. It is here assumed that the process goes on at the ordinary atmospheric temperature.

When, however, calcium carbonate is deposited from solution at a high temperature, it usually crystallizes as aragonite and not as calcite. This is the case at certain hot springs, as for example at the Sprudel at Karlsbad in Bohemia (temp. 163° F.) and to some extent at Bath (120° F.). At Karlsbad there is now being formed an extensive deposit of pisolite, in which the individual pisoliths, up to 3 or 4 mm. in diameter, are composed of concentric shells of crystalline aragonite with tangential structure. A similar deposit is also formed at Vichy, in France. Strange as it may seem, it appears that in some instances the actual deposition of the carbonate from such hot springs is due to the action of algæ or of bacteria.

A very similar type of pisolitic or oolitic structure may, however, be produced by wholly inorganic means ; if a nucleus, such as a sand grain or a tiny fragment of shell is kept in a continual state of movement by gentle currents in a saturated solution of calcium carbonate, it may be covered by concentric coats of carbonate, forming oolitic grains : such a process has been observed in the Great Salt Lake of Utah : even here, however, it is possible that calcareous algæ have taken part in the process.

Nitrates. It has long been known that nitrates exist to a greater or less extent in all fertile soils, their presence being due to the action of bacteria : thus their occurrence is hardly a matter that concerns the geologist. Rain-water also contains a very small amount of nitric acid, due to electrical discharges in the atmosphere. However, deposits of solid nitrate of any considerable size are decidedly rare. Sodium and calcium nitrates have been found in certain arid regions, and also in caves in the western United States, in some cases in association with boron compounds, as in certain salt-lake deposits. The only really important commercial source of nitrates is the nitrate of soda (Chile saltpetre) of northern Chile. The origin of these remarkable deposits has given rise to much discussion and the problem must be regarded to a large extent as still unsolved.

The nitrate region lies in the northern provinces of Chile at a high elevation and in one of the driest areas of the world. The salt-beds are found at the surface or under a thin covering of soil, and not always at the lowest points in the neighbourhood. On the contrary they sometimes lie on slopes or even form a capping to ridges, hence they cannot have been formed by evaporation of pools of water.

To explain their presence many ingenious theories have been put forward. The presence of combined nitrogen has been attributed to the decomposition of vast masses of sea-weed, or of guano, as well as to electrical action in the atmosphere during thunderstorms or during fogs. It is known that many volcanoes give out compounds of ammonia. The sea-weed theory implies an enormous elevation of the land, but the presence of iodine in the salts affords some evidence in its favour. Oxidation of guano seems to be excluded by the complete absence of phosphoric acid in the salts, and the electrical causes adduced hardly seem adequate.

The most satisfactory discussion of the genesis of the Chilean nitrate deposits is that given by Singewald and Miller.[1] After enumerating the different classes of explanations put forward to account for the deposits, the authors say that in their opinion most of these theories contain a certain amount of truth, though no one of them will explain everything. The presence of iodine, however, is no proof of direct origin from sea-weed, since all oxidized silver ores in arid regions include silver iodides (e.g. Broken Hill, N.S.W., to quote a non-American instance). Hess has shown that in arid regions all ground-waters contain a small amount of nitrate, doubtless carried down from the soil, where it is produced by bacteria, or perhaps to some extent derived from the atmosphere. In the Chilean nitrate region both climate and ground-water conditions are exceptionally favourable to the accumulation of such nitrates. Both the west winds blowing in from the sea and the east winds from the Andes are relatively very dry, since both are rising in temperature when they reach the nitrate area. This is an elevated plain or broad valley between the coast ranges and the Andes, and in spite of the arid climate ground-water from the Andes is everywhere very near the surface, sometimes only 3 or 4 feet down in the salt pans (salars), more often some 20 feet. Hence capillarity is very active, owing to the tremendous evaporation, and soluble salts are deposited in large quantities in the soil and subsoil.

It so happens that sodium nitrate is a particularly deliquescent salt, and will therefore tend as it were to climb out of the wetter places and salars by a process of efflorescence ; it is found on the lower slopes of the western hills, and even on knolls and mounds in the salars.

The original source of the nitrogen is to be sought in the decomposition of organic matter in the soil, to some extent perhaps in guano-dust blown in from the coast, and probably to some extent in atmospheric nitrogen brought into combination during thunderstorms in the higher Andes. Each of these causes alone seems inadequate, but all taken together over a long period of time would doubtless be able to produce the necessary effects.

The Carbonates. One of the most important groups of minerals occurring as rock-builders is that including the carbonates of the alkaline earths and iron. Of these calcite is by far the commonest, but dolomite and iron carbonate are also very abundant, both in sediments and in vein-deposits. Some iron carbonate (siderite) is perhaps of direct magmatic origin, but this need not be considered here.

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[1] Singewald and Miller, *Econ. Geol.*, vol. xi, 1916, pp. 103–114, with bibliography.

The first group of the carbonates includes those that crystallize in the rhombohedral system ; calcite, dolomite, magnesite, siderite, rhodochrosite and various mixtures of some of these, forming solid solutions (ankerite, breunnerite, etc.). These last are not very important geologically ; for their properties and occurrences reference may be made to a textbook of mineralogy. But the paragenesis of the first four in the above list has to be considered somewhat carefully. The second group of carbonates includes aragonite, witherite and strontianite. Only the first of these is of geological importance.

The Rhombohedral Carbonates. It must first be observed that in this group calcite stands somewhat by itself : it crystallizes in the class having the highest degree of symmetry, and therefore shows somewhat complex and peculiar forms, such as the scalenohedron, not found in the other members of the series. It is also important to note that calcite does not form mixed crystals to any notable extent with magnesium carbonate : certainly not more than 1 per cent. of $MgCO_3$ being dissolved under the most favourable artificial conditions. On the other hand there appear to be continuous mixed crystal series between calcite, siderite and rhodochrosite, although little is known of the crystallographic and physical properties of the middle members.[1] The possibility of mixed crystals between calcite and siderite especially is of importance in the study of iron ores, and requires further work. Calcite is often found of a pink tinge, probably due to dissolved manganese carbonate.

Modifications of Calcium Carbonate. It is well known that calcium carbonate occurs in nature in two different crystalline forms, calcite and aragonite, differing in their physical and crystallographic properties. Aragonite, which has the higher density, is the less stable under normal atmospheric conditions and therefore more soluble than calcite, into which it is easily converted by a slight rise of temperature or increase of pressure. It is therefore never found in rocks that have undergone even a small degree of metamorphism. Nevertheless the available facts as to the thermal relations of these two minerals are curiously contradictory and difficult to explain in a rational manner. It may be well to state first that it is apparently possible for $CaCO_3$ to exist in four modifications, viz., vaterite, aragonite, calcite and α-$CaCO_3$. Of these vaterite has only been prepared artificially : it is clearly less stable than aragonite and is of no geological significance, so far as is known. The α-form will be referred to later.

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[1] Leitmeier, in Doelter's *Handb. d. Mineralchemie*, vol. i, p. 274.

The chief difficulties in the interpretation of the relations of calcite and aragonite are these. Firstly, although aragonite has the higher density, or smaller specific volume, nevertheless it changes to calcite on increase of pressure, as in dynamic metamorphism. This appears to be inconsistent with the principle of Le Chatelier, or van't Hoff's law. Secondly, calcium carbonate crystallizes from hot saturated solutions as aragonite, from cold solutions as calcite, although in thermal metamorphism an increase of temperature changes aragonite to calcite. Other peculiarities are noticeable in the occurrence of these two minerals in calcareous organic structures: thus corals are always aragonite, and echinoderms are always calcite; some mollusca have both, in different layers of the same shell. The nacreous layers of lamellibranch shells, as also pearls, are aragonite, and so on. There cannot be much difference in the physical conditions of deposition of these various structures, and the whole thing still awaits explanation.

It is found that when calcite is heated to 970° C. under a pressure sufficient to prevent any dissociation it undergoes a reversible change to another modification, α-$CaCO_3$, the change being indicated by a well-marked heat-effect. It has not yet been found possible to determine the physical and optical properties of the α-form, which can only exist inside a closed bomb. This inversion may, however, be of importance in metamorphism of pure limestones, though what its practical effect may be is entirely unknown. At any rate it appears to be completely reversible.

$$\beta\text{-}CaCO_3 \overset{970^\circ}{\rightleftharpoons} \alpha\text{-}CaCO_3$$

Dolomite. The most difficult problem connected with the carbonates is undoubtedly that of the origin of dolomite rock or magnesian limestone, which occurs in enormous masses in many formations, as for example the Cambrian of the N.W. Highlands, the Permian of N.E. England, and the Trias of the Tyrol. The Carboniferous Limestone of England is also extensively dolomitized in places. Some of these were evidently formed originally as normal open-sea limestones (Cambrian and Carboniferous): the Alpine Trias consisted largely of coral reefs, while many modern reefs are extensively dolomitic in their lower parts (Funafuti boring). The Permian Magnesian Limestone, however, was formed in an inland sea of the Caspian type and is therefore rather exceptional. The study of these deposits naturally raised the question of the mode of origin of such rocks, and the problem has been attacked on the experimental, chemical side, as well as by field work.

The mineral dolomite has the composition $CaMg(CO_3)_2$, which may also be written $CaCO_3.MgCO_3$. It therefore becomes essential to decide whether it is to be regarded as a solid solution of the calcium and magnesium carbonates, calcite and magnesite, or whether it is a molecular compound. Now the rule states that in solid solutions the physical properties of the series can be expressed as linear functions of the composition, while in molecular compounds this is not the case. If then some physical constant for calcite, dolomite, and magnesite is plotted against the composition (for example, the specific volume, $1/D$), the three points thus obtained should lie on a straight line. When this is done, this is found to be the case (see Fig. 38). On the other hand mixed crystals showing other compositions within the series $CaCO_3$–$MgCO_3$ are not known, and dolomite crystallizes in a class of the rhombohedral system differing from that in which calcite is found : the evidence is therefore inconclusive. It may be that dolomite is actually an instance of a molecular compound with no volume change and no heat effect in its formation : if so it is an exceptional case.

Many attempts have been made to produce dolomite synthetically, but it must be admitted with very little success, since the temperatures and pressures that had to be employed before any useful results were obtained were far beyond those likely to occur for example in modern coral reefs, or indeed in the later stratigraphical systems. And even then the result was usually a mere mechanical mixture of calcium and magnesium carbonates and not the mineral dolomite. The idea underlying most of these researches is that sea-water contains a considerable proportion of magnesium salts, and therefore under certain conditions a reaction may occur between these salts and calcite, leading to the formation of the double carbonate :

$$2CaCO_3 + MgCl_2 = CaMg(CO_3)_2 + CaCl_2$$

If the magnesium is supposed to exist as sulphate, then the result will be the formation of gypsum, or possibly of anhydrite if the temperature is high enough (see p. 180).

$$2CaCO_3 + MgSO_4 + 2H_2O = CaMg(CO_3)_2 + CaSO_4.2H_2O.$$

It is suggested that in the lagoons of coral atolls the temperature may rise sufficiently high to enable this reaction to go on to a considerable extent, and it certainly is a fact that both modern and ancient coral reefs are considerably dolomitized ; this was shown very clearly by the careful study of material obtained from deep borings made within the lagoon of the Funafuti atoll in the

Indian Ocean.[1] The Triassic dolomitized reefs of the Tyrol have been already mentioned. Skeats[2] has also carried out valuable work on this subject, his main conclusion being that dolomitization is most active in warm seas at depths down to 150 feet, corresponding to a pressure of about 5 atmospheres. It is important to notice that corals consist of aragonite, which is much less stable than calcite and therefore more readily attacked by magnesian solutions.

The Carboniferous Limestone of England is also considerably dolomitized locally, and it has been noticed that this is specially prone to occur in the neighbourhood of large open joints, where water can circulate freely, and that the limestone is often also considerably stained red by iron. It is supposed that this is due to the percolation of strong saline solutions from overlying salt lakes of the Triassic period, when the climate was doubtless very hot as well as dry. In certain parts of the Carboniferous Limestone of Derbyshire and northern England (Weardale, Alston Moor and Allendale) lead and zinc ores occur in extensive "flats." The ores here extend out along the bedding-planes of the limestone from veins and fissures, the process being one of replacement, and the limestone forming the matrix of these metalliferous flats is usually very dolomitic.[3] Here the origin of the dolomite-rock is undoubtedly to be attributed to metasomatism, though the source of the magnesium is not indicated.

There is, however, evidence that in some cases at least dolomite is primary: it has been observed in small but well-formed rhombohedral crystals in certain Triassic marls.[4] In some instances dolomite is found in association with rock-salt and gypsum, or anhydrite, indicating primary formation in salt lakes from saturated solutions of calcium and magnesium carbonates; as in the Trias of Thüringen and Württemberg. According to Trechmann this is also the case with the Permian Magnesian Limestone of Durham. There has been much discussion of the origin of this great dolomite-rock formation, which is of so much importance both as a flux in metallurgical processes and as a building stone. Trechmann concludes that a very large part at any rate of the dolomite is of primary deposition from saline lakes, extremely rich in dissolved calcium and magnesium salts, and not, as has been so often suggested, due to infiltration of magnesian solutions into normal limestones.[1] It seems clear that the Magnesian Limestone as a whole originated in a basin of the Caspian type, since it contains marine fossils, and that this basin became more and more desiccated, till finally the highly arid conditions of the Trias supervened. During the Permian period, as a result of the Armorican-Pennine folding, great areas of Carboniferous Limestone were undergoing denudation and there is no difficulty in accounting for the presence in this sea of a large amount of dissolved calcium carbonate: the source of the magnesium is less clear, but it is well known that all salt lakes contain magnesium salts in large amount, whatever its origin may be.

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[1] "The Atoll of Funafuti," *Report of the Coral-reef Committee of the Royal Society*. London, 1904.

[2] Skeats, *Quart. Journ. Geol. Soc.*, vol. lxi, 1905, p. 97.

[3] Smith, Stanley, and Carruthers, R. G., *Spec. Rep. Min. Res. Gt. Britain*, vol. xxv, 1923, p. 76, and vol. xxvi, 1923, p. 10. These flats at Boltsburn in Weardale and at Nenthead are mainly confined to the Great Limestone, where they may extend hundreds of feet from the feeding vein.

[4] Cullis, C. G., *Rep. Brit. Assoc.* Leicester 1907, p. 506. See also Wade, *Quart. Jour. Geol. Soc.*, vol. lxvii, 1911, p. 245.

The mineral dolomite also occurs to a large extent as an infilling of veins, metalliferous or otherwise: it is specially common in association with ores of lead and zinc, and with copper. In such cases the dolomite has clearly been directly deposited by solutions, sometimes of deep-seated (hydrothermal) origin, sometimes perhaps by circulating meteoric waters. The physical chemistry of the origin of such deposits is evidently simple crystallization from saturated solutions, either on fall of temperature or on escape of carbon dioxide owing to relief of pressure, much like the formation of stalactites and travertine.

Sometimes dolomite-rocks are converted by metamorphism into marbles, especially by pressure, just like limestones. This subject, which is of great interest, is treated somewhat fully in Chapter VII.

Dolomite and ferrous carbonate appear to possess very considerable, if not complete, mutual solubility, but these will be more conveniently considered later.

Ferrous Carbonate. The mineral form of this compound, variously known as chalybite or siderite, is common in nature, and often of considerable commercial importance as an ore of iron. It often occurs in a more or less earthy or amorphous form, much mixed with various impurities, frequently as nodules or concretions, and is in many cases the chief constituent of the so-called clay ironstones. It also occurs to a considerable extent as a constituent of oolitic ironstones, usually associated with a green silicate of iron (chamosite). There has been much discussion as to the primary or secondary character of much of the iron carbonate in such rocks, some authorities regarding it as a primary crystalline precipitate from saturated solutions, while others attribute its presence to metasomatic replacement of limestone, by reaction between calcite or aragonite and iron-bearing ground-water. The balance of opinion now inclines towards a primary origin for the iron of the oolitic ores, though the details of the process are unknown. The action of bacteria has been suggested as a possible cause. Some important iron ores, such as the hæmatites of Cumberland and Lancashire, have undoubtedly been formed by replacement of calcite or dolomite, but it is uncertain whether the replacement took place in two stages, first to $FeCO_3$ and then to Fe_2O_3, or directly without intervention of iron carbonate.

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[1] Trechmann, C. T., "On the Lithology and Composition of the Durham Magnesian Limestones," *Quart. Jour. Geol. Soc.*, vol. lxx, 1914, especially pp. 249 and 259. Garwood, E. J., *Geol. Mag.*, 1891, p. 433.

A specially interesting case is that of the ferruginous rocks of the Lake Superior from which the workable ores have been derived by concentration of iron. The primary rocks in their unaltered condition consist of chert, green iron silicate rocks (greenalite) and crystalline iron carbonate. It is now suggested that all of these have been produced by precipitation on the floor of the sea of compounds derived from magmatic solutions that were related to the eruption of the associated submarine volcanic rocks: this accounts well enough for the silica and iron, but the source of the carbon dioxide is not apparent.

The carbonates of lime, magnesia, iron and manganese appear to form a very complete series of mixed crystals (solid solutions) of the double salts of the dolomite series, the various end-compounds being $CaCO_3.MgCO_3$, $CaCO_3.FeCO_3$, $CaCO_3.MnCO_3$, $MgCO_3.FeCO_3$, and so on. Many varieties of these occur in nature, and are very often described by the general name of ankerite, a term which has no very precise meaning, but indicates mixed carbonates of Ca, Mg, Fe, possessing so far as is known the dolomite symmetry. Such carbonates, as well as calcite, dolomite, siderite and rhodochrosite are very common forming part of the *gangue* or non-metalliferous filling of ore-veins: sometimes such masses of siderite are worked as iron ores.

The Orthorhombic Carbonate Series. Besides calcium, the related metals barium, strontium and lead have carbonates with orthorhombic symmetry, witherite, strontianite and cerussite, forming with aragonite a natural isomorphous group. So far as is known, however, the last three are not dimorphous.

Most of the special points of interest connected with the physical chemistry of aragonite have been discussed in the previous section. It only remains to add a few words as to its occurrence in nature. Besides organic aragonite, the mineral is also found to a considerable extent in ooliths and pisoliths, especially in those formed in hot springs, and it is not uncommon as a vein-mineral along with metalliferous ores. This suggests that these veins were filled by hot solutions. A curious stalactitic or coral-like form is often called *flos-ferri.* Its general appearance suggests deposition from colloidal suspension. A variety of crystalline aragonite has been found containing up to 8 per cent. $PbCO_3$, indicating solid solution with the cerussite molecule. In this purely geological work it is unnecessary to discuss the occurrence of witherite, strontianite and cerussite, all of them minerals of considerable economic importance, especially cerussite, which is common in the upper, oxidized portions of lead veins, being formed from galena, probably in two stages, thus:

$$\begin{aligned} PbS + {}_2O_2 &= PbSO_4 \\ PbSO_4 + CO_2 + H_2O &= PbCO_3 + H_2SO_4 \end{aligned}$$

The reason for the second reaction is that $PbCO_3$ is very much less soluble than $PbSO_4$, and is therefore precipitated readily from dissolved sulphate.

CHAPTER X

ORE DEPOSITS

Nature of Ore Deposits. The origin and relationships of the natural deposits of the useful metals is a subject of the highest interest, involving for its proper elucidation the application of many well-known physical and chemical principles, but space will not permit of an adequate treatment, which requires a whole book to itself. In this chapter an attempt will be made to state only a few of the principal factors involved in modern theories of mineralization.

At the outset a clear distinction must be drawn between primary and secondary ore-deposits, and for the present attention will be confined to the first-named group.

The primary ore-deposits are those which still remain in the position in which they were first formed, and to a great extent, often wholly, in their original chemical combinations. Frequently, however, it is found that in their upper parts, exposed to surface geological agents, certain definite changes have taken place, without the ore having been removed beyond the limits of the original body. Here are comprised mainly the phenomena of oxidation and secondary enrichment, as defined later. The secondary ore-deposits of the usual classification are those which have been worked over by various geological processes, often involving transport and re-deposition, or even solution and re-precipitation. Many of this class form, or are enclosed by, ordinary sediments, usually of more or less recent date and superficial occurrence.

In the first place it is now generally agreed that most, if not all, primary ore-deposits are of direct magmatic origin: they are in fact products of the normal processes of differentiation of magmatic solutions, such as have been already described in an earlier chapter. But they clearly belong to special phases of differentiation and to some extent to special types. In order to make the matter clear it is necessary to introduce at this point, somewhat abruptly, a most important and far-reaching generalization, as follows:

from basic magmas the metallic ores tend to separate first, and to sink to the bottom: from acid magmas they tend to separate last and to rise to the top. This difference of behaviour is correlated with the presence in or absence from the magma of fluxes with which the metals can form volatile compounds, or in which they are freely soluble down to low temperatures. In the gabbro-basaltic magmas fluxes are not abundant, while the ores occur mainly as sulphides. Hence two-phase differentiation by limited miscibility of silicates and sulphides comes into play; the magma separates into two layers, sulphides below and silicates above. These fractions may either consolidate in place, or they may be separately drawn off before consolidation and injected elsewhere as independent intrusions. It must be remembered that in most cases the sulphide fraction will be far smaller in bulk than the silicate fraction: it may form only small veins and masses and may even be squeezed by earth movements into the overlying gabbro, since the freezing-point of sulphides is apparently lower than that of basic silicates. There are known, however, many large masses of sulphides; pyrite, chalcopyrite or pyrrhotite, of a size measurable even by hundreds of yards, such as those of the Huelva district in S.W. Spain, of Norway and of the Urals. These actually form bodies comparable in size to many gabbro laccoliths. Another interesting case is that of the platinum metals, which are always found along with chromium in peridotites and serpentines. These ultrabasic bodies appear to be themselves differentiates of larger basic magmas.

Turning now to acid magmas, we find a very different state of affairs. It is well known that nearly all the tin of the world is found in primary association with tourmaline granites; it is closely accompanied by tungsten, molybdenum, arsenic and other metals, and often, less closely, by copper, zinc, lead and silver. Now the tourmaline-granite type of magma is clearly characterized by the presence of an excessive amount of fluorine and boron, as well as by much water, the last product of differentiation being a highly siliceous solution rich in these constituents. In such a solution the tin probably exists as fluoride at a high temperature; as the temperature falls this reacts with water according to the following equation:

$$SnF_4 + 2H_2O \rightleftharpoons SnO_2 + 4HF.$$

The mineral cassiterite has actually been made synthetically by this reaction, and it is highly probable that tungsten, which forms a still more volatile fluoride WF_6, boiling at 19°, is also precipitated in a somewhat similar manner. Even in these deposits, however, sulphides are present in some quantity and molybdenite, MoS_2, is a common accompaniment of the ores just named.

In many places, as in Cornwall, the tin-tungsten group of ores are succeeded in an upward direction by copper sulphides, and these again by zinc, lead and silver, forming a system of zones surrounding granite intrusions in successive shells. There are of course no hard and fast dividing lines, but the zones grade into one another imperceptibly.[1]

A careful and intensive study of this subject in America, based on generalizations drawn from a large number of different areas has led to the establishment of a rather more extended and complete zone-succession, in substantial agreement with that seen in Europe, but containing other zones not here represented. The following is the scheme as elaborated by Spurr: [2]

7. The zone of earthy gangues, barren of valuable metals.
6. The zone of silver and much gold, with Sb, As, Bi, Se and Te.
5. The galena zone.
4. The blende zone.
3. The cupriferous pyrite zone.
2. The free gold-auriferous pyrite zone.
1. The pegmatite zone with Sn, W and Mo.

To this classification as given by Spurr one more zone might well be added, between (6) and (7), since in some places, especially in California, ores of mercury can even now be seen in process of formation by deposition from hot springs, almost at the surface. It is curious that in England both the gold-bearing zones are missing.

It should be mentioned that the non-metallic minerals also show a similar and more or less parallel arrangement: in the lower zones quartz is dominant, with tin and copper, while with lead and zinc barytes and fluorspar are much more characteristic, often with dolomite and siderite. The highest zones of all are often again rich in silica, which is frequently not quartz, but some chalcedonic or opaline form. The very abundant gold-quartz veins appear to represent in most cases the most acid differentiate from magmas of intermediate or sub-acid type; that is, monzonites, tonalites and granodiorites rather than the typical acid granites. Gold is however found to a greater or less extent in a great variety of rocks, both acid and basic. Copper is perhaps even more ubiquitous in its occurrence and cannot truly be said to be characteristic of any particular type.

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[1] Davison, *Geol. Mag.*, vol. lviii, 1921, pp. 505–512. Cronshaw, *Trans. Inst. Min. Met.*, vol. xxx, 1921, pp. 408–449.

[2] Spurr, *Econ. Geol.*, vol vii, 1912, p. 489.

There has been much discussion as to the precise state of combination in which the metals travel outwards from the magmatic solutions, and the question is even now undecided. It is commonly believed that the heavy metals tin and tungsten are extracted as fluorides, as before described, and the very common association of lead and zinc ores with fluorspar, as in Derbyshire and Cumberland, is also very suggestive in this respect, although there is actually nothing to show that these metals travel as fluorides. On the other hand a great number of metals commonly occur as sulphides, while arsenides are also very common, as in the case of nickel and cobalt, and in a less degree copper. The sulpharsenide of iron, mispickel, is also a very common mineral in vein-deposits. However, it has recently been suggested by Morrow Campbell that the chief agent in this process has really been silica, probably in a hydrated form, this silica being regarded as the most acid differentiate of the magmas.[1] A subject still in need of investigation is the possible occurrence in magmatic solutions of compounds of silico-fluoric and boro-fluoric acids, most of which appear to be soluble in water and highly volatile.

However this may be the fact remains that it is quite clear that the metals are somehow extracted from igneous magmas by some process of differentiation. The question of their exact state of combination in the final stages is not of much importance, since in all probability when first they begin to travel outwards the temperature is so high that the vapours are dissociated, and combination into compounds will only occur later. At any rate it is clear that very few, if any, of the valuable metals, except iron, actually occur in nature as silicates. Sulphides and analogous compounds are much more common, while the list of metals that occur as oxides is quite limited.[2]

According to this view, then, at a certain stage in the differentiation of an intrusion, when the greater part of the rock has already solidified, there are residual, highly siliceous solutions or vapours (fluids) tending to travel outwards along radial cracks and fissures and carrying the metals in the free state or more probably in combination with boron, fluorine, sulphur, arsenic, etc. These fluids travel along the temperature gradient, and eventually reach a point at which they begin to crystallize. Since the freezing points of such compounds vary, it is easy to see how a zonary arrangement is produced, the distance attained by each compound from the source being controlled by its freezing point under the given conditions.

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[1] Morrow Campbell, *Trans. Inst. Min. Met.*, vol. xxx, 1921, pp. 3–27. Abstract in *Mining Mag.*, vol. xxiii, 1920, pp. 306–10.

[2] Reference is here made only to primary deposits: oxides and oxygen-salts are very common among secondary products in mineral veins, as explained later.

Contact and Replacement Deposits. Since these fluids extracted from the magma contain elements of great chemical activity, it is a natural conclusion that well-marked reactions will occur between them and the surrounding rocks, especially at and beyond the margin of the intrusion. The resulting phenomena are thus intimately connected with metamorphism, especially with the metasomatic type. In this respect rocks show a very varying degree of susceptibility to change, the group of limestones being most easily affected, the aluminous rocks, clays and shales rather less so, while the pure quartz rocks are very stable and little altered. Consequently replacement ore-bodies are very common in limestones and are usually associated with the common lime-silicates, garnet, idocrase, wollastonite, diopside, etc., so often found in non-ore-bearing altered calcareous rocks in similar situations. Many instances are known where limestones and dolomite rocks have been more or less bodily replaced by sulphides and other ores along igneous contacts. The reactions involved are in some cases evidently highly complex and the final products are controlled by conditions of temperature and pressure. On the details of this subject, however, we possess little or no positive information, and there has been much vague and rather unprofitable discussion as to the occurrence of bodily replacement, especially by sulphides, on a large scale.

Genetic Classification of Primary Ore-Deposits. On the basis of the facts briefly outlined above it is possible to draw up a scheme of classification of the primary ore-deposits, founded on the geological principle of depth from the surface, which of course is actually equivalent to a classification by temperature and pressure at the time of formation. The categories thus obtained are as follows :

A. Magmatic segregations and concentrations within the limits of the intrusion.

B. Pegmatitic segregations in veins and dykes, with the so-called pneumatolytic gangue-minerals and quartz, felspar and mica.

C. Deep-seated high temperature veins : gangue mainly quartz.

D. Veins of intermediate depth, with quartz, barytes and fluorspar.

E. Shallow veins, with dominant carbonate gangue minerals.

The following are a few examples, chosen at random, of each type :

A. Tinstone, and molybdenite in granites ; copper and nickel sulphides in norites ; chromite and platinum in peridotites.

B. Wolfram in granite-pegmatites; rare earths in syenite-pegmatites; apatite in gabbro-pegmatites.

C. Copper-quartz veins; auriferous pyrite and arsenopyrite veins (Brazil); lead-zinc-silver-rhodonite lodes (Broken Hill type).

D. Lead-zinc veins with barytes and fluorspar (Derbyshire).

E. Veins with antimony, arsenic, mercury (Tuscany and California).

It must of course be understood that these divisions are arbitrary and as in nature there are no hard and fast lines, innumerable transitional types exist. Nevertheless this classification does seem to correspond largely to the facts and to express in a simple way the genetic relationships of the primary ore-bodies on a purely physical basis.

Distribution of Ores in Time and Space. This is a subject of very great theoretical interest and practical importance, but covering too much ground to be discussed here at any length. For details reference must be made to some book on ore-deposits in general. The broad general principles alone can be stated; namely, that just as there are petrographical provinces and petrogenetic epochs, so also there are metallographical provinces and metallogenetic epochs. Furthermore there is a close connection between them. A particular igneous episode, if metalliferous at all, which is by no means always the case, usually shows certain distinctive features of ore-deposit. Thus the Armorican petrographic province of Devon and Cornwall is specially characterized by tin and tungsten in the lower zones, with copper, zinc and lead above: the Tertiary eruptives of Transylvania carry gold tellurides: the Tertiary province of Bolivia carries tin, tungsten, bismuth and rich silver ores; the late Mesozoic and early Tertiary intrusions of Montana and of Arizona are both specially rich in copper; the late pre-Cambrian basic rocks of northern Ontario show veins of silver, nickel and cobalt ores, and so on indefinitely.

Secondary Changes in Ore Deposits. When mineral veins and other forms of ore-deposits are exposed by denudation they come under the influence of potent chemical agents, especially water and the oxygen of the atmosphere, and various secondary changes are set up. The uppermost layers of the crust are characterized especially by active water circulation and the presence of free oxygen. Further down the rocks are usually saturated with stagnant water and the conditions are reducing rather than oxidizing. Hence a double set of processes may take place. Some ore-minerals, such as tinstone and native gold and platinum, are so stable that they are little affected, but the majority of them undergo oxidation, hydration or solution, or various combinations of these processes. The ordinary phenomena can be most clearly explained by a brief consideration of the events in a vein of copper pyrites, for example. Water and oxygen readily decompose chalcopyrite and a somewhat complicated reaction occurs: the iron forms hydrated ferric oxide, after passing through the stages of ferrous and ferric sulphates: the copper oxidizes direct to soluble cupric sulphate. The reaction is usually represented by the following equations, on the assumption that, as is nearly always the case, pyrite is present as well as chalcopyrite:

$$\left.\begin{aligned} CuFeS_2 + 4O_2 &= CuSO_4 + FeSO_4 \\ FeS_2 + H_2O + 7O &= FeSO_4 + H_2SO_4 \end{aligned}\right\}$$

$$\begin{aligned} 2FeSO_4 + H_2SO_4 + O &= Fe_2(SO_4)_3 + H_2O \\ Fe_2(SO_4)_3 + 4H_2O &= Fe_2O_3.H_2O + 3H_2SO_4 \end{aligned}$$

The final result therefore is a precipitate of solid iron oxide and an acid solution of copper sulphate. The same reaction can also be represented in a general way, as follows, without any attempt to produce an exact equation.

$$\begin{tikzcd} \left.\begin{matrix} FeS_2 \\ CuFeS_2 \end{matrix}\right\} \arrow[r] \arrow[d] & FeSO_4 \arrow[r] & Fe_2(SO_4)_3 \arrow[r] \arrow[d] & Fe_2O_3.xH_2O \\ CuSO_4 & & H_2SO_4 & \end{tikzcd}$$

This form is the more satisfactory in view of our scanty knowledge of the intermediate reactions.

The iron oxide thus formed remains in place as an *iron cap* or *gossan* on the surface and often provides a useful indication of the presence of a metalliferous lode below. The fate of the copper sulphate solution must now be considered: it must be regarded as circulating in the lode, with a general downward tendency. Nearly all natural waters contain carbon dioxide, which precipitates copper salts from solution as basic carbonates; also if the solution comes in contact with calcareous minerals, especially calcite or dolomite, a double decomposition occurs.

$$\begin{aligned} & CuSO_4 + CaCO_3 + H_2O = CuCO_3.Cu(OH)_2 + CaSO_4 \\ \text{or}\quad & CuSO_4 + CaCO_3 + H_2O = 2CuCO_3.Cu(OH)_2 + CaSO_4 \end{aligned}$$

giving rise to the well-known minerals malachite and azurite; the conditions that determine the formation of one or other of these carbonates are not known. Under laboratory conditions the green malachite is always obtained, but azurite is almost equally common in nature.[1]

In the case of lead sulphide (galena) the usual secondary minerals are anglesite, $PbSO_4$, formed by direct oxidation, or the carbonate, cerussite, $PbCO_3$, the latter being the more common. Since zinc sulphate is a very soluble salt it does not occur as a mineral, but zinc carbonate, calamine, and the hydrated silicate hemimorphite $Zn_2SiO_4.H_2O$ are the usual oxidation ores. Silver also shows similar phenomena, and silver chloride, AgCl, is found in large quantities in some dry regions where the ground-waters are saline. Under similar circumstances copper may also form a basic chloride, atacamite, as in Chile. In the cobalt and nickel arsenide veins, a not uncommon type, the arsenates erythrite and annabergite are the usual oxidation products. The possible varieties of oxidized ores are endless, and the foregoing must serve as examples. Certain changes in iron ores, of great practical importance, are discussed elsewhere (see p. 213).

As the above-named oxidized solutions are continually passing downwards in the lode, part of the metallic contents may escape precipitation and eventually reach the water-table, the level of permanent ground-water, where the conditions are on the whole reducing, and the reaction alkaline rather than acid. In this zone two kinds of processes occur. The oxidized salts may be reduced to a lower state of oxidation ; for example, cupric sulphate may be reduced to cuprous sulphide, Cu_2S (chalcocite), or other copper salts to cuprous oxide, Cu_2O. (cuprite, ruby copper) or the reduction may go still further, to the native metal, especially with copper and silver. Native mercury, bismuth and arsenic are also fairly common, but tin, zinc and lead do not occur as metals.

Very commonly, however, reactions take place between the solutions and the primary sulphides in the zone of reduction, leading to the formation of secondary sulphides, such as bornite, Cu_3FeS_3 or $3Cu_2S.Fe_2S_3$ as it may also be written. This appears to be formed by reaction with pyrite. Secondary chalcopyrite is also found, and in all probability secondary blende and galena can be precipitated on the primary crystals. Furthermore mineral lodes are nearly always complex, carrying traces at least of antimony, arsenic, bismuth, etc. These combine readily with the copper, silver, or lead, for example, forming numerous secondary sulphantimonides and sulpharsenides, such as tetrahedrite, tennantite, ruby silver ores, stephanite, jamesonite, bournonite, and innumerable others. Hence arises a zone rich in metals just at and below the permanent water-level. This is called the *zone of secondary enrichment* and is often the most profitable part of a vein.

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[1] The writer has made many attempts to prepare azurite artificially, but as yet without success. The copper carbonate produced by the action of $CuSO_4$ on limestone is always the green malachite. Dana (*Textbook of Mineralogy*, 1922, p. 451) says azurite has been formed by keeping a solution of copper nitrate in contact with calcite for several years.

Mineral Formation in Ore-Deposits. The general principles controlling the actual deposition of the minerals in a vein or lode, both metallic and non-metallic, are exactly the same as those already dealt with in connection with the crystallization of the igneous rocks : the determining factors are temperature, pressure and concentration, and the systems involved, when not too complex, can be dealt with according to the thermodynamic principles summed up in the Phase Rule. In most cases, however, the number of components and phases is large, and data scarcely exist for the detailed discussion of particular cases. This remark applies specially to the formation of primary ores, where the former presence of volatile constituents of unknown character is often to be suspected. The reactions involved in oxidation and secondary deposition are simpler and have in some cases been reproduced experimentally, as previously explained.

Since there is every reason to believe that the formation of mineral deposits commonly went on very slowly and probably from very dilute solutions in many cases, plenty of time was available for the establishment of a true equilibrium and for the operation of the inversions appropriate to the variations of temperature and pressure, as in metallic alloys. Hence ore-minerals when examined by the same methods as employed for the study of metals, often show very similar structures, especially those characteristic of molecular changes after solidification, such as the separation of solid solutions into an intimate mechanical mixture of two or more components, and the writer believes that many microphotographs published as showing replacement of one mineral by another are in reality examples of this effect.[1]

A point of some interest has arisen in connection with the quartz of vein-deposits. It has been shown that in the granites and quartz-porphyries the quartz belongs to the β-form, whereas in pegmatites and vein-deposits the plagihedral α-quartz is found.[2] Since the inversion-point is known to be at 575°, this gives us at any rate an upper limit of temperature for the formation of mineral veins. This fact is in entire agreement with the general idea that they are deposited by magmatic fluids at comparatively low temperatures, since the quartz is precisely similar in general character to that of the pegmatites.

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[1] For this phenomenon there is no neat English name exactly equivalent to the German *Entmischung*.

[2] Wright and Larsen, *Amer. Journ. Sci.*, vol. xxvii, 1909, p. 421.

A very large number of the common ore minerals of the metals belong to the category of mixed crystals, or solid solutions: it is comparatively rare to find an ore-mineral, especially among the sulphides, corresponding exactly to a simple chemical formula. Thus copper minerals nearly always carry at least traces of silver and gold, and often payable quantities. A good deal of silver, gold, platinum and other metals are now obtained from the slimes remaining in the tanks in the electrolytic purification of copper. Native gold is always naturally alloyed with more or less silver, and the telluride gold ores are always mixed crystals of gold and silver tellurides. Nickel and cobalt nearly always occur together, and most iron ores carry more or less manganese. Examples of such types of isomorphism are endless and are of considerable technical importance. One further example will alone be mentioned. In the island of Cuba are vast deposits of an oxidized iron ore, formed by decomposition of serpentine and containing chromium and nickel in such proportions that it is practicable to smelt them direct to pig-iron and to produce at a cheap rate a natural chrome-nickel-steel of a type which is now largely used for constructional purposes on a large scale, for example for bridges and girders. Many of these mixed ores are of the highest value; such as the very well-known association of silver with lead, a fact which has been utilized at any rate since the time of the Romans and probably much earlier. Small values in gold also often add greatly to the profits of copper mines. In other cases, however, the mixture may be deleterious, as with copper in iron, and highly complex ores are not generally popular with metallurgists on account of the expense of smelting. An extreme case is the enormously costly extraction of minute traces of radium from uranium ores.

Molecular Compounds in Ore Minerals. In the last section we dealt only with mechanical mixtures or solid solutions of different ore-minerals. It is clear, however, that many complex ores, e.g. sulphides, can be regarded as true intermolecular compounds of two or more simple end products. This subject can best be illustrated by a concrete example, the best for the purpose being the so-called sulphantimonides of copper, silver and lead. These may be regarded as molecular compounds of Cu_2S, Ag_2S or PbS, with Sb_2S_3. (It is to be noted that all the four compounds just named occur also as simple minerals, chalcocite, argentite, galena and antimonite.) In the case of copper and lead three intermolecular compounds are known, while silver has no less than five. These may be tabulated as follows:

Chalcostibite, $Cu_2S.Sb_2S_3$	Miargyrite, $Ag_2S.Sb_2S_3$	Zinkenite, $PbS.Sb_2S_3$
—	—	Jamesonite, $2PbS.Sb2S_3$
Bournonite, $3(Cu_2,Pb)S.Sb_2S_3$	Pyrargyrite, $3Ag_2S.Sb_2S_3$	—
Tetrahedrite, $4Cu_2S.Sb_2S_3$	—	—
—	Stephanite, $5Ag_2S.Sb_2S_3$	Geocronite, $5PbS.Sb_2S_3$
—	Polybasite, $9Ag_2S.Sb_2S_3$	—
—	Polyargyrite, $12Ag_2S.Sb_2S_3$	—

In no case is the series complete, so far as known, but the number of such compounds is surprisingly large. Unfortunately data do not exist as yet for the construction of full freezing-point curves for any of these series, but the general form that such curves must take has already been discussed (see p. 29). As a further point of interest it may be noted that in many instances the corresponding arsenic minerals are known, such as tennantite, $4Cu_2S.As_2S_3$ and proustite $3Ag_2S.As_2S_3$. Many of the minerals just named are rather rare, but some, such as tetrahedrite, tennantite, pyrargyrite, proustite and stephanite, are important ores of copper and silver belonging to the zone of secondary enrichment.

Secondary Ore Deposits. From the physico-chemical standpoint the true secondary ore-deposits do not show much that is of interest. Their formation is due to the ordinary processes of denudation and deposition and in the great majority of cases the occurrence of the minerals is due merely to their high degree of stability, both chemical and physical. Reference is here made chiefly to such things as gravels carrying gold, platinum or tinstone, all of which are almost unaffected by chemical agents, while tinstone also possesses the extra advantage of great hardness. There are also known in many places deposits of sand consisting largely of magnetite or ilmenite, along with garnet, rutile, zircon, tourmaline and other non-metallic minerals, which are both stable and heavy: very similar are the sands found on the coasts of Brazil and southern India with a large proportion of monazite; these are now exploited as sources of thorium and cerium for gas mantles. The origin of such sands is almost entirely a mechanical process, mostly due to sorting by moving water, streams, waves and currents and closely analogous to many processes employed in ore-dressing.

To the geologist the most interesting of the sedimentary ore deposits are the ironstones, by far the most important sources of iron at the present day. The ironstones of the British Coal-measures, about which we hear so much in school-books and examination-papers, and so little in the official statistics of production, are excellent examples of iron ores of direct sedimentary origin, which have undergone little or no change since their formation. They are in fact fossil bog-iron ores, and it is strongly suspected that their origin is mostly due to bacteria, though on this subject further research is required.

It is impossible here to give an account of the origin of all types of ironstone. Two only will be selected, comprising by far the greater part of the world's output, namely the hæmatite ores of Lake Superior and the oolitic ores of England and Lorraine. In the year 1913, these three areas produced as follows:

	Tons.
Lake Superior	52,377,000
Lorraine	48,000,000
England	12,566,000

The iron ores of the Lake Superior region are of peculiar type; they belong essentially to the group of crystalline schists. The history of their formation is believed to be as follows. At various periods during the Pre-Cambrian there were laid down great thicknesses of more or less ferruginous cherty sediments; as to the origin of these there has been some dispute, but it is now generally considered that the iron and silica were probably derived from magmatic solutions poured out on the sea-floor in connection with basic eruptions. Thus were accumulated great thicknesses of iron carbonate and iron silicate rocks, with cherts. At a later date these were uplifted and subjected to subaerial denudation, which led to leaching out of the silica and concentration of the iron compounds in impervious basins, usually due to folding or faulting. Still later there was pronounced metamorphism and the iron compounds were largely converted to hæmatite, generally banded and still showing traces of the original bedding. It is only in the areas where this natural concentration occurred that workable ores are found; the concentration was not, as often stated, due to the metamorphism, but to ordinary weathering. The ores are therefore residual, the enrichment being due to removal of more soluble constituents, including silica, and not to transport by ferruginous solutions introduced during crust-disturbances.[1]

By far the most important iron ores of Europe are the Jurassic ironstones of England and Lorraine, the latter being the foundation of the great German iron and steel industry. All these ores are highly phosphoric and therefore their use only reached full development after the introduction of the basic process by Thomas and Gilchrist of Middlesbrough, with the help of Dr. J. E. Stead, in the early eighties. There is no doubt that the approaching exhaustion of the German portion of the Lorraine iron field was one of the proximate causes of the Great War of 1914–18, as it was essential for the maintenance of the industry that Germany should obtain control of further supplies of ore.

In England the chief deposits of oolitic ores are in the Cleveland district (Middle Lias), north Lincolnshire (Lower Lias), Leicestershire and Oxfordshire (Middle Lias), south Lincolnshire, Rutland and Northamptonshire (Inferior Oolite). In the year 1917 the output of these counties was as follows:

	Tons.
Cleveland	4,809,861
Northamptonshire	3,169,110
Lincolnshire	2,699,532
Leicestershire	937,707
Oxfordshire	434,435

These together account for 80 per cent. of the total British production of iron ore. Of the remainder 10 per cent. came from the hæmatites of Cumberland and Lancashire (Lower Carboniferous) and 8 per cent. from the Coal-measures.

The origin of these ores has been a matter of much discussion, and the question is still unsettled. Broadly speaking there are two theories: first that the ores were originally deposited much as we now see them in depth, and second, that they have been formed by metasomatic replacement of oolitic limestones.

At first sight the second theory appears to have much to recommend it and was long accepted almost without question, but there are certain difficulties to be stated later. This view, as being the older, will be considered first.

In the first place it is quite clear that these ironstones are marine sediments: they are regularly interbedded with shales, clays, sandstones and limestones of normal type, they are often full of well-developed, healthy-looking marine fossils, not by any means stunted, but often very large, and the oolitic structure is essentially the same as in the oolitic limestones. When fresh and unweathered however, they consist of blue or grey iron carbonate (siderite) or a green iron silicate, or a mixture of both, while the fossils are often still calcite or aragonite. When examined microscopically it is often found that the ooliths differ in composition from the shell fragments and ground-mass. Thus in many cases the ooliths are iron carbonate or silicate, or even iron oxide, while the ground-mass is calcite. Again the ooliths may be silicate or oxide, while the ground-mass is siderite. These facts suggest a progressive replacement in such a way that the ooliths are more advanced in alteration than the ground-mass. Now it is well known that in oolitic limestones the ooliths are often aragonite while the cement is calcite, and aragonite is less stable than calcite; hence the following scheme has been suggested:

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[1] Leith, C. K., *Economic Aspects of Geology*, New York, 1921, pp. 167–170.

	Stage I.	Stage II.	Stage III.
Ooliths	Aragonite	Siderite	Oxide
Groundmass	Calcite	Calcite	Siderite

This scheme however takes no account of the silicate, which is so common, and in sections of the Cleveland stone it is sometimes seen that the ooliths are calcite in a ground-mass of siderite. Nevertheless it is very common to find ooliths and fossils consisting of oxide in a ground-mass of calcite or chalybite.

The common occurrence of green iron silicate seems easy to account for when it is remembered that oolitic grains in limestones usually possess a skeleton of opaline silica, soluble in alkalies, and are therefore unstable, while similar skeletons can easily be isolated from ironstones by treatment with acid. It is not unreasonable to suppose that circulating solutions of iron could attack the silica and convert it to ferrous silicate.

Of late years careful observations on many oolitic ironstones, especially the Wabana ore of Newfoundland (Ordovician), have tended to show that the precipitation of iron as silicate or carbonate was contemporaneous with the formation of the deposit.[1] The evidence cannot be given here in detail, but it certainly suggests that in this instance the ooliths when lying loose on the floor of the sea already consisted of ferruginous compounds. It is difficult to see how the flourishing fauna now represented by the fossils of the British ironstones managed to live in a solution of iron salts strong enough to cause active precipitation of iron silicate, and unless the solutions were fairly strong, near saturation, it is not clear why precipitation should occur in these particular beds, which are often sharply marked off above and below and may pass laterally within a short distance into sediments almost free from iron.

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[1] Hayes, A. O., *The Wabana Iron Ore of Newfoundland*, Canada Dept. of Mines, Geol. Survey, *Memoir* 78, 1915.

Secondary Changes in Oolitic Ironstones. A glance at any ironstone quarry in the Midlands will show that the stone differs in colour and general composition at the surface and in depth. This marked change is brought about by meteoric waters. Near the surface the stone consists mainly of hydrated brown oxide; fossils are usually represented by hollow casts only, and grains of quartz are often conspicuous. In its broad outlines the change consists in a leaching out of the calcium carbonate and oxidation and hydration of the iron compounds. This leads to a concentration of iron and silica with concomitant removal of lime. Consequently the weathered stone becomes richer in iron, with more silica and alumina. Some of the calcareous unweathered ores, as in north Lincolnshire and Oxfordshire, contain sufficient lime to be self-fluxing, or even contain more lime than is needed, while the weathered Northampton stone needs addition of limestone in the blast furnace. A good furnace charge can often be obtained by mixing them in proper proportions, thus saving quarrying and transport of limestone. The Cleveland ore is rather high in alumina and requires a good deal of flux. For this purpose Magnesian Limestone from Durham is largely used. The phosphorus remains in the weathered ore, since iron phosphate is very insoluble. The Lorraine ores are commonly rather higher in iron than the British, and very high in phosphorus. From all of these "basic slag" is obtained as a valuable by-product. The large supplies of phosphatic manure thus obtained have been of invaluable service on the naturally rather poor soils of Germany in conjunction with the Stassfurt potash salts.

CHAPTER XI

REFRACTORIES AND ABRASIVES

Definitions. A very large number of technical processes of the highest industrial importance depend on the use of materials of a specially resistant nature for the construction of their plant and equipment. A few examples of such are furnace-linings, glass pots, crucibles, asbestos packings, to name only a small number selected from widely different fields : in point of fact the varieties of apparatus so used are innumerable. It is necessary to include here not only materials resistant to high temperature, but also those little or not at all affected by chemical agents and therefore suited for the construction of industrial chemical plants on a large scale. From these we pass by a natural transition to the field of ceramics, the manufacture of porcelain, china, pottery and earthenware, which again is closely allied to brick and tile making. The raw materials for all these and other cognate industries may be conveniently grouped under the general heading of refractories, although some of them, e.g. common brick clay, are not truly refractory in the strict technical sense. It is convenient to include in the same category a few other substances, such as the moulding sands used in iron and steel works for the preparation of castings, and sands used in glass-making, although with these resistance to fusion is not the primary quality sought. A rather modern development is the manufacture of chemical ware from pure fused silica, instead of glass.

The geologist is not concerned with the technical details of the processes here employed, but rather with the origin and sources of the raw materials and the modifications that they undergo in the processes of manufacture, the latter mainly as bearing on the conditions governing the character and durability of the final product and its suitability for the purposes in view. In this field the results of petrographical and mineralogical investigations conducted in recent years along purely theoretical lines have proved to be of the highest practical importance, as leading to efficiency and economy on an industrial scale, as well as revealing new sources of material in hitherto unknown directions. During the war this branch of the subject became of the greatest national importance, since before that time British manufacturers had been to a large and very undesirable extent dependent on foreign supplies, and home resources of many materials for various reasons had been almost wholly neglected, as for example in such a comparatively simple matter as sands for glass-making, especially for the higher qualities and optical glass. Another noteworthy example is magnesite for furnace linings, which came almost entirely from what during the war were enemy countries, or regions largely controlled by the Central Powers. In this and other instances supplies were eventually developed within the Empire. It is impossible, however, to discuss here the interesting political and fiscal questions involved in this subject.

General Classification of Refractories. The substances included in this category regarded in the narrow sense as those resistant to high temperature and chemical action can be most conveniently classified on a chemical basis. We thus obtain three principal groups, namely:

(1) Acid; (2) neutral; (3) basic.

(1) *The Acid Group.* By far the most important member of this group is silica, either free or in various forms of combination as silicates; among the latter especially a number of somewhat complex minerals known as the aluminosilicates. Here are to be included quartz in all its varied geological occurrences, a few simple silicates, such as sillimanite, enstatite and the asbestiform minerals and the aluminosilicates, of which the purest forms are found in various clays (china clay, fire clays, etc.). The felspars, though not highly refractory, must also be included here.

(2) *The Neutral Group.* Here are comprised a small number of substances neither acid nor basic in their chemical characters, and notable mainly for their inertness and resistance to chemical action: the chief are chromite and graphite.

(3) *The Basic Group.* These substances are notable for their power of resistance to high temperatures, but they are all strongly basic in their chemical behaviour, and most are readily attacked by acids to form salts. They include bauxite, lime and magnesia.

It is not proposed here to discuss the origin of the natural resources of these refractories from the geological point of view, but rather to deal with their composition and properties in the natural state, and more especially with the changes that take place in them during manufacture and use.[1] These changes involve some points of great interest from the standpoint of physical chemistry and mineralogy, and their investigation has in its turn thrown much light on problems of petrology and petrogenesis.

The Forms of Silica and their Thermal Relations. One of the most interesting and important, and at the same time one of the most complicated of the single-component systems of geological significance is afforded by the exceedingly common substance silica. As is well known, silica constitutes on analysis about 60 per cent. of the whole accessible portion of the earth's solid crust. The greater part of this doubtless exists in combination as silicates, but nevertheless free silica is extremely abundant, occurring as quartz in the more acid igneous rocks ; as quartz, chalcedony, opal and many other cryptocrystalline and amorphous forms in mineral and other veins ; and as quartz, chert and flint in sediments. Many of the amorphous forms of silica, however, either are or were originally binary systems of silica and water, belonging properly to the category of colloids : these are treated elsewhere under their proper heading, and in this section attention is confined to the definitely crystalline forms and to their behaviour under varying conditions of temperature and pressure.

Quartz is certainly one of the commonest of minerals ; perhaps the most widely distributed of all, after felspar. But it is now known that crystalline silica exists in at least two other forms, known as tridymite and cristobalite, with quite distinct crystallographic and physical properties : furthermore, each of the three has been shown to be capable of existing in at least two forms, each stable only within a definite range of conditions, and undergoing transformation from one to the other under appropriate treatment : it is still an open question whether chalcedony is an independent mineral, but the balance of what evidence is available suggests that it is.

All this is by no means only of academic interest : it has acquired great and increasing importance owing to the widespread use of silica in various forms in a great range of industrial processes : from the present point of view the chief of these is the employment of silica as the raw material in the manufacture of various refractory products, and especially silica-bricks for furnace linings. Consequently a great amount of research has recently been devoted to the elucidation of the thermal relations and transformations of the different forms of silica, and especially at high temperatures. In industrial processes on a large scale it is essential to be able to predict the behaviour of the materials under given conditions and the nature and properties of the final product. In the case of silica this can now be done. It is unnecessary to enumerate here any of the technical processes, such as glass-making, where the silica enters into combination in complex systems: we are only here concerned with its behaviour in a one-component system. It may be well, however, to mention that silica when fused and quickly cooled may solidify as a glass, which is apparently stable under a wide range of conditions, and possesses certain useful properties (e.g. silica-glass laboratory ware). Under proper heat-treatment, however, this glass is easily made to crystallize.

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[1] For a comprehensive account of British resources of refractories reference may be made to the following Memoirs of the Geological Survey : *Special Reports on the Mineral Resources of Great Britain*, vol. vi, 2nd edition, 1920 ; vol. xiv, 1920 ; vol. xvi, 1920 ; vol. xxviii, 1924. For Glass Sands, see Boswell, P. G. H., *British Resources of Sands and Rocks used in Glass-Making*, 2nd edition, Longmans, 1918.

As already stated by far the most abundant of the crystalline forms of silica is quartz. Tridymite is only moderately common, while cristobalite is, so far as we yet know, a distinctly rare mineral. Chalcedony is also common, but is often difficult to distinguish from some of the apparently non-crystalline or cryptocrystalline forms, except by detailed microscopical examination. The density of chalcedony is nearly the same as that of quartz, but tridymite and cristobalite both have a much lower specific gravity and therefore greater specific volume. This fact is doubtless of importance as affecting the possibility of inversions under certain conditions, and quartz would naturally be the stable form at high pressures. The inversion temperature would also be raised by pressure, just as the change from solid to liquid (i.e. fusion) is affected by pressure. It appears that in every case the inversion from the low to the high temperature form is accompanied by an increase in the crystallographic symmetry of the mineral: some examples of this will be mentioned later.

In any discussion of the transformations of the forms of silica under varying temperatures it is necessary to emphasize very strongly the fact that the velocity of these inversions is in most cases very slow, the only exception being certain low-temperature changes in tridymite and cristobalite, which are pretty rapid and easily reversible. The changes in quartz and the high-temperature inversions between the three minerals are exceedingly sluggish, and the state of equilibrium establishes itself very slowly indeed. In consequence of this many silica products consist of mixtures of all three minerals, at least two of them being in reality in an unstable condition and perhaps all three. In exactly the same way both tridymite and cristobalite are found in natural rocks that also contain quartz. It is evident then that all three minerals possess very wide fields of metastable equilibrium. The practical result is that a number of the different forms can all exist together apparently for an indefinite time: at any rate there appears to have been no transformation in certain Tertiary lavas, which contain both quartz and tridymite. Silica glass can easily be devitrified by holding it for a considerable time at a temperature a little below its softening point, but as it is entirely an artificial product we have no information as to its possible behaviour over long periods of geological time.

The most complete investigation of the stability relations of the silica minerals is that carried out by C. N. Fenner[1] at the Geophysical Laboratory in Washington. This author found that the relations between the species quartz, tridymite and cristobalite are in every case enantiotropic, that is to say reversible. The inversion temperatures have been determined accurately within a very few degrees:

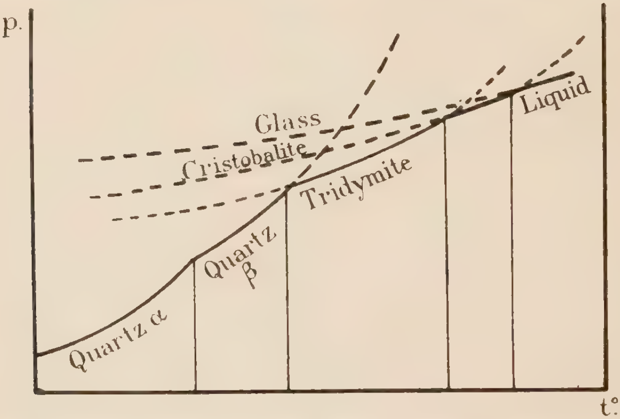

Fig. 59.—Thermal diagram for the forms of silica. Somewhat simplified from Fenner, *Amer. Jour. Sci.*, vol. xxxv, 1913, p. 331, the low-temperature inversions of tridymite and cristobalite being omitted. Broken lines represent unstable states.

quartz ⇌ tridymite at 870° ± 10°
tridymite ⇌ cristobalite at 1,470° ± 10°

therefore at all temperatures below 870° quartz is the only really stable form: natural tridymite and cristobalite must be in an unstable (metastable) form. It is likewise found, however, that each of them when prepared artificially can be kept for an indefinite time at lower temperatures, each of them undergoing also an inversion to other forms of different crystal symmetry at quite low temperatures, 117° for α-tridymite to β_1-tridymite, 163° for β_1-tridymite to β_2-tridymite, while α-cristobalite changes to β-cristobalite at some temperature between 274° and 224°, according to its previous heat-treatment.

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[1] Fenner, C. N., *Amer. Jour. Sci.*, vol. xxvi, 1913, pp. 331–348.

Of more general geological interest, however, are the relations of the two forms of quartz. The low-temperature form, α-quartz, possesses trapezohedral symmetry, that is to say, a principal trigonal axis and three diad axes in a plane at right angles to the principal axes and lying at 120° to each other. These elements of symmetry give rise to the peculiar zones of faces distinguishing right-handed and left-handed individuals: the optical properties are also peculiar, involving rotation of the plane of polarization of a beam travelling along the principal axis; the direction of rotation corresponding to the right- and left-handed crystallographic symmetry. This is the kind of quartz found in mineral veins and pegmatites, and in it the trapezohedral faces of the right- and left-handed individuals are often clearly distinguishable. Such crystals also often show complicated forms of interpenetration twins.

When α-quartz is heated to 575° it inverts to β-quartz, a form with a higher degree of symmetry and distinctly lower refractive indices and weaker double refraction. This is the form found in granites and quartz-porphyries. In granites quartz is usually the last mineral to solidify and therefore shows no crystal-form, but in quartz-porphyries it commonly occurs as simple hexagonal bipyramids with little or no development of the faces of the prism. Since it is in reality a high temperature mineral this variety is not stable in nature, but it preserves its simple external form and is readily identifiable.

The change of the physical properties of quartz at the inversion point is admirably illustrated by exact measurements of the refractive indices, as shown in the diagram Fig. 60. Not only is there a sudden drop in the value of the refractive indices, but the rate of variation with temperature changes its sign, that is, up to 575° the refractive indices decrease with rise of temperature; above that point they increase, so that the slope of the curve is reversed. The strength of the double refraction also undergoes a distinct change, being less in the β-form and nearly constant, while in the α-form it decreases notably as the temperature rises.[1]

From what has just been said it is clear that quartz can be used as a geological thermometer: at any rate the form present in a rock shows whether the rock has been crystallized above or below

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[1] Rinne and Kolb, *Neues Jahrb. für Min.*, 1910, Pt. II, p. 150.

575° C. The facts here disclosed are in entire agreement with evidence derived from other sources as to the temperatures prevailing during the formation of pegmatites and mineral veins, including the ore-deposits. In many instances a metalliferous pegmatite dyke lying in a granite has been traced laterally and continuously, with a regular change of mineral composition into a pure or nearly pure quartz vein lying in the country rock at a considerable distance from the granite, where the temperature must have been fairly low at the time of its formation. Many quartz-veins, either metalliferous or barren, are undoubtedly of direct magmatic origin, having been formed by residual watery solutions extracted from the cooling magma. The minerals deposited from such complex solutions must have low freezing points, but no direct evidence is available as to the effect, if any, of water and other substances on the inversion point of quartz.

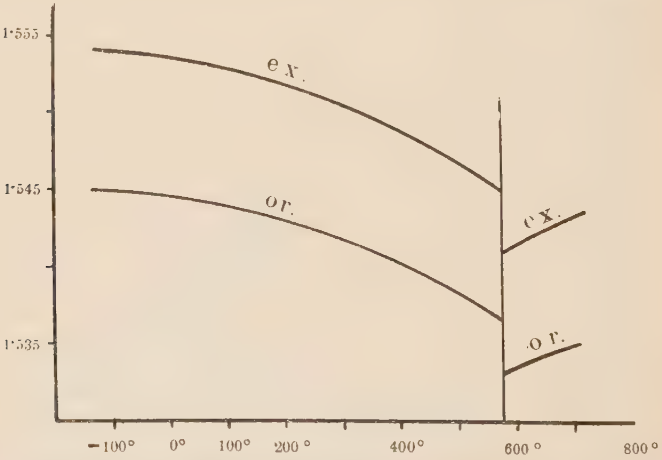

Fig. 60.—Changes in the refractive indices of quartz for D_2 line with varying temperature.

(*ex* = extraordinary, *or* = ordinary ray.) From Rinne and Kolb, *Neues Jahrb.*, vol. ii, 1910, p. 150.

Silica as a Refractory. By far the commonest form of silica is quartz and this mineral is often found in large amounts in a state of great purity, as sands, sandstones or quartzites. The purest forms of loose incoherent quartz sands are mainly used for glass-making, and hearth sands, while for furnace linings and similar purposes the hard rocks are crushed and made into bricks with some suitable binding material.

Perhaps the best known of all such silica rocks are the ganisters of the Sheffield district: to these alone should the name ganister strictly be applied, but its meaning is now extended to cover rocks of similar character from various other sources; many rocks coming into the category of quartzites are also used. Most of these come from various horizons in the Carboniferous system in northern England, Wales and Scotland, but mention may also be made of the Hartshill quartzite, Nuneaton (Cambrian); the Highland quartzite (Pre-Cambrian); and the Moor Grit of the N.E. Yorkshire moors (Jurassic). Many of the ancient metamorphic quartzites of the Highlands and Ireland would be quite suitable, but transport is deficient.

For a good quality ganister or silica rock the main requirement is a high silica percentage: the rock should be as nearly as possible pure quartz, since any other constituent tends to lower the softening-point. The following selected analyses of a few well-known types show how nearly they approach to purity.[1]

	Ganister. Sheffield.	Quartzite. Guiseley, Yorks.	Millstone Grit. W. Butsfield, Durham.	Ganister. Lealholm, Yorkshire.	Quartzite. Kidwelly, Carmarthen.
SiO_2 . . .	97·02	98·72	98·22	97·58	97·55
Al_2O_3 . . .	·34	·65	·43	·26	·72
Fe_2O_3 . . .	·31	·10	·37	·82	·41
CaO . . .	·05	tr.	·16	·05	·02
MgO . . .	·13	·01	·04	·19	·03
K_2O . . .	·09	·14	·07	·12	·23
Na_2O . . .	·17	·41	·10	·14	·12
H_2O . . .	·44	·28	·28	·18	·43
FeS_2 . . .	·49	—	—	—	—
C	·44	—	·14	·02	·04

In the manufacture of silica bricks the ganister and other rock is first crushed to the required degree of fineness and then mixed with a bonding material. The selection of this bond is a matter of the greatest importance. Its object is two-fold, to cause the brick to harden on burning and to produce the conditions most favourable to the conversion of as much as possible of the quartz to tridymite. This conversion causes an increase of volume, and it is desirable that as much as possible of the expansion should take place during the manufacture of the brick itself, and not afterwards during its use in the steel furnace. The bond most commonly used is milk of lime. This substance acts in two ways: it combines with the silica to form calcium metasilicate $CaO.SiO_2$ (pseudowollastonite) [1] and it favours the quartz-tridymite inversion, which takes place more rapidly in contact with a silicate melt than on plain heating of pure quartz. As shown by Rankin and Wright,[2] the eutectic point between SiO_2 and $CaSiO_3$ lies at 1,436°, hence when this temperature is reached the added lime combines with some of the silica to form a small amount of liquid of the composition 63 per cent. SiO_2 and 37 per cent. lime. However, most silica rocks contain a little alumina (and other impurities). Hence it is necessary to consider the three-component system $CaO–Al_2O_3–SiO_2$. The ternary eutectic for $CaSiO_3$, SiO_2 and Al_2O_3 lies as low as 1,165°. Therefore in this case formation of liquid begins much earlier in burning. Sometimes a little alumina is added to facilitate this result; generally, however, enough is present. It is found by experience that with a high quality silica rock the addition of about 2 per cent. of lime gives the best results, and it may be considered that the ideal mixture contains about 97 per cent. SiO_2, 1·2 per cent. Al_2O_3 and 1·8 per cent. CaO. The usual burning temperature is about 1,500°.

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[1] Thomas, Hallimond and Radley, *Spec. Rep. Min. Res Gt. Britain* (Mem. Geol. Survey), vol. xvi, 1920. These analyses are here somewhat simplified by the omission of some of the less important constituents; consequently the sum is in most cases below 100.

After burning the brick is found to have increased considerably in volume and when examined microscopically is seen to consist of an aggregate of grains of quartz, more or less converted to tridymite on their edges, embedded in a ground-mass consisting of a felted aggregate of crystals of lime-silicate and tridymite. It is this ground-mass that gives coherence to the brick.

Since the tridymite-cristobalite inversion point lies at 1,470° bricks burned at temperatures above that figure should in theory contain cristobalite, but in practice this change is very slow in occurring.

We must now consider very shortly what further changes take place in the bricks when used in a steel furnace where the temperature may be as high as 1,700° in places. Under such conditions the surface of the bricks exposed to the gases is corroded away with some rapidity, and a marked reaction occurs between the brick and the finely-divided iron oxide always present in the furnace gases. After a brick has been in use some time, so that some 3 inches or so have been cut away by corrosion, it is usually possible to recognize three distinct zones: first a light coloured band 1 to

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[1] If lime is present in excess, other silicates would be formed (see p. 143). but in silica bricks this is never the case, so the point need not be considered,

[2] Rankin and Wright, *Amer. Journ. Sci.*, vol. xxxix, 1915, pp. 1–79.

$1\frac{1}{2}$ inches thick, largely composed of cristobalite, then a broad dark brown or black band, very rich in magnetite, and with the silica mainly as tridymite, with some lime-silicate and unaltered fragments of ganister. Beyond this there is little change except a pale brown coloration.

The actual floor of the furnace in contact with the molten steel is composed of very pure quartz sand and a bank of the same material extends some distance above the level of the molten metal with its slag covering. The temperature of the molten steel is about 1,600° or a little more, consequently, after use the uppermost layer of the sand bed consists mainly of cristobalite embedded in slag. Here for a small depth the inversion seems to be pretty complete. Below this comes a hard mass of interlacing crystals of tridymite, often with many cracks and interstices filled with a fayalite slag.[1]

Fire-clays and China-clay. Although all clays may in a sense be considered as refractories, it is unnecessary for our present purpose to consider such ordinary processes as the making of bricks, tiles and drain-pipes. For these purposes almost any common clay can be used with more or less success. Attention will here be confined to certain products in which purity and a high degree of refractoriness are the essential features.

China Clay or Kaolin. It has already been pointed out in Chapter VIII, p. 155, that the common product of the decomposition of alkali felspar, orthoclase or albite, is a substance having the composition $Al_2O_3.2SiO_2.2H_2O$: when crystalline this is called kaolinite, when amorphous, halloysite. Some difference of opinion prevails as to how this substance is to be regarded from the chemical point of view : some authorities consider it to be a hydrated silicate of alumina, while others look upon it as an alumino-silicic acid. This point is not, however, of much practical importance.

The chief source of kaolin is the decomposition of granite : good examples are found in Devon and Cornwall, and may be taken as typical. It is a matter still open to discussion as to whether the kaolinization of the Cornish granites should be regarded as a process of pneumatolysis, or merely as a special type of weathering : in support of the former view may be mentioned the fact that kaolinization is often most strongly developed where other signs of gas-action are most marked, such as tourmalinization and greisening. On the other hand a similar change undoubtedly takes place in felspars as a result of weathering at the ordinary temperature, though not to such great depths or on so extensive a scale.[1]

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[1] The substance of the foregoing section is condensed from a very complete discussion of this subject by Thomas, Hallimond and Radley, *Spec. Rep. Min. Res. Gt. Brit.*, vol. xvi, to which reference should be made for further details and some good illustrations.

Pure kaolin is an extremely refractory substance and cannot be made into porcelain alone ; it is mixed with quartz and felspar, very often approximately in the proportions of one-half kaolin, one-quarter quartz, and one-quarter felspar. The quartz diminishes shrinkage, by its own expansion on inversion, and the felspar acts as a flux, lowering the fusion point. For specially resistant porcelains for chemical work, alumina is added. The actual change that takes place on firing is essentially vitrification.

Fire-clays. In technical and popular writings and in a large proportion of serious geological literature the term fire-clay is used in a very broad sense to cover a large number of natural deposits of widely varying composition. Some of them are true clays, of exceptional purity, while others approach very closely in composition to true silica rocks. In fact some of the Sheffield ganisters are known in the trade as " best clay." Broadly speaking all fire-clays are distinguished by the presence of a considerably higher proportion of silica than corresponds to the ideal clay as defined in the foregoing paragraph. Hence they are properly placed in the category of acid refractories.

In order to attain a sufficiently refractory character, a clay used for the manufacture of fire-bricks should contain as little as possible of constituents other than silica and alumina. The alkalies, lime and iron all have a marked effect in lowering the fusion point, although magnesia is less objectionable in this respect. In a good fire-clay the total of such impurities should not exceed 3 per cent.

The analyses opposite, selected from the memoir quoted in the footnote,[2] show the chemical composition of typical examples of certain well-known fire-clays.

It is doubtful to what extent the definite compound kaolinite or halloysite is to be regarded as present in the more common types of clay ; at any rate it is certain that they are far from pure and must contain many other compounds as well, perhaps to some extent in the colloidal form. Microscopic examination under the highest powers that can be used shows the presence in most if not all clays of particles of quartz, mica and other minerals down to the limit of

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[1] Reid and Flett, *The Geology of the Land's End District*, Mem. Geol. Survey, 1907, p. 58. Scrivenor and Jones, *The Geology of South Perak*, Geol. Dept., F.M.S., 1919, pp. 28–31.

[2] Ennos, F. R., and Scott, A., *Refractory Materials, Fireclays, Analyses and Physical Tests*. Spec. Rep. Min. Res., vol. xxviii, Mem. Geol. Survey, 1924. (In copying these analyses a number of minor constituents have been omitted, so that in all cases the totals are considerably below 100, which of course is not the case in the original publication.)

	Better Bed Fire-clay. Leeds.	Fire-clay. Penistone, Yorks.	Mountain Mine Clay, Rishton, Lancs.	Fire-clay. Consett, Durham.	Fire-clay. Cwmbran, Monmouth.	Fire-clay. Glencryan, Glenboig.
SiO_2 . .	53·14	77·86	47·15	57·32	70·53	51·30
Al_2O_3 .	28·74	13·05	33·82	26·71	18·09	29·42
Fe_2O_3 .	1·85	1·36	2·31	1·39	1·14	2·12
CaO . .	·15	·28	·50	·18	·17	·48
MgO . .	·53	·14	·76	·72	·71	·49
K_2O . .	·70	·65	·96	2·31	1·87	·18
Na_2O .	·24	·24	·39	·05	·17	·14
H_2O . .	12·18	6·54	13·39	9·50	5·88	13·84

visibility, and some staining material, such as iron oxide, iron sulphide or carbon is always present.[1] Nevertheless it is convenient to regard kaolinite as being the true *clay-constituent* of even many very impure clays, other substances being present in mechanical mixture or held by adsorption.

The theoretical chemical composition of pure kaolinite is as follows :

Silica	46·5
Alumina	39·5
Water	14·0

or approximately $SiO_2 : Al_2O_3 : H_2O = 46 : 40 : 14$.

These figures can be used as a sort of standard clay-substance in considering the amounts yielded by analyses of other clays, as will appear shortly.

The Constitution of Clays in General. Most common clays contain in addition to the ideal pure clay substances kaolinite or bauxite considerable amounts of sand, flakes of mica and other resistant minerals, as well as carbonates, carbon, sulphides and innumerable other things in small quantities. Some clays of the purer kind, however, approximate to hydrated mixtures of silicates of alumina, some having excess of silica and others excess of alumina. This subject has been dealt with by G. V. Wilson,[2] who divides clays into two principal classes : kaolinitic clays with excess of silica and bauxitic clays with excess of alumina. This author has introduced a diagrammatic method of representing these relations. Fig. 61 gives a somewhat simplified form of his diagram : it is constructed as follows.

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[1] See various papers by W. M. Hutchings, *Geol. Mag.* for 1891, 1894, 1896.

[2] Wilson, G. V., *The Ayrshire Bauxitic Clay*, Mem. Geol. Survey, Scotland, 1922, p. 6 and Fig. 2.

The composition of kaolinite is SiO_2 46·5, Al_2O_3 39·5, H_2O 14·0 per cent. The water is ignored and alumina plotted against silica on two rectangular co-ordinates. The point K thus represents pure kaolinite. Join OK and divide into 100 parts. Through K draw a line making with OA an angle θ such that $\tan\theta = \frac{46·5}{39·5} = 1·177$; whence $\theta = 49°\,40'$, and cutting the axes OA and OS in X and Y. Then $XK = KY$. Draw lines parallel to OK as shown. These lines then give the excess in percentages of Al_2O_3 or SiO_2 over the kaolinite ratio for any sample plotted on the diagram. The point where the alumina line or the silica line cuts the diagonal OK shows the percentage of potential kaolinite and the horizontal or vertical distance from this point to the original point of intersection of the alumina and silica lines gives the amount of free alumina or free silica present. These can be read off directly from the graduations provided along OK and the axes.

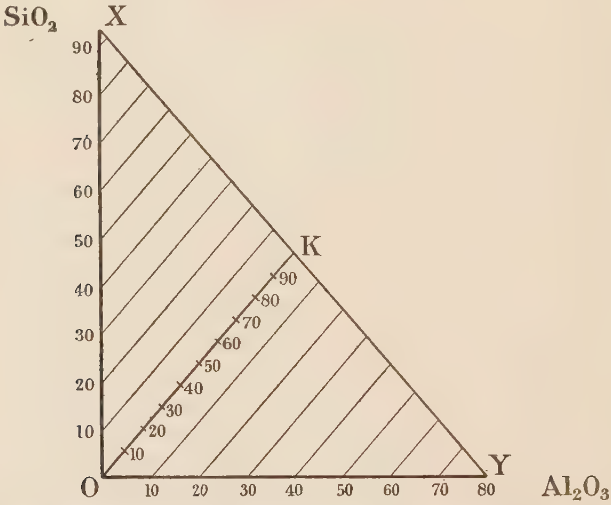

FIG. 61.—The composition of fire-clays, as explained in the text.

We arrive then at the conclusion that a fire-clay is to be regarded as a variety of clay in which the sum total of constituents other than silica, alumina and combined water does not exceed 3 per cent. On the other hand, the ratio of silica to alumina varies within wide limits. The minimum percentage of silica is 46 in pure china-clay and from this figure it may rise almost indefinitely and the most acid fire-clays grade imperceptibly into ganister and silica-rock.

Microscopic examination of siliceous fire-clays easily shows the presence of much quartz sand. A small proportion of the silica is also combined with the alkalies and other oxides present as detrital mica, felspar and other minerals. The rest of the combined silica exists in clay-substance, either kaolin or something similar.

On this basis it is possible to construct a diagram to show the constitution of different samples of fire clay, as shown in Fig. 62. The two rectangular co-ordinates are each divided into 100 parts.

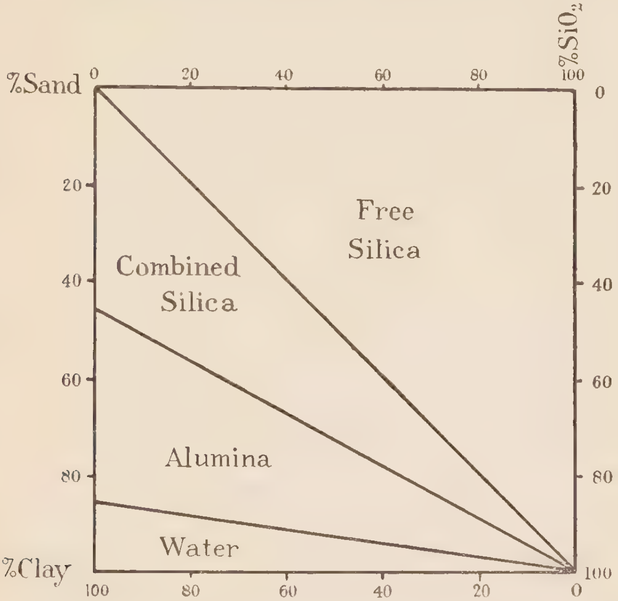

FIG. 62.—The composition of kaolinitic and bauxitic clays.
Slightly simplified from Wilson, *The Ayrshire Bauxitic Clay*, Mem. Geol. Survey, 1922, p. 7.

On the left-hand ordinate are plotted the composition of ideal clay, viz. H_2O 14·0, Al_2O_3 39·5, SiO_2 46·5. Lines drawn from these points to the opposite corner will show the proportion of true clay mixed with sand in more siliceous clays. The diagonal of the square separates the total silica into free silica (quartz) and combined silica in clay. Thus knowing the total silica percentage of a mixture of kaolin and sand the diagram automatically gives the proportion in which each is present. It can thus be used to test the purity of a clay from the analysis in the following way: on the right-hand ordinate mark off from the top the total silica percentage: from this point draw a horizontal line to cut the middle inclined line: the vertical through this point gives the correct proportions of free and combined silica, alumina and water in such a mixture of sand and clay. The more nearly the given figures for alumina and water fit this ratio, the purer is the clay. The percentages of sand and clay in it are read off along the top and bottom axes of the diagram.

The great majority of the British fire-clays belong to some division of the Upper Carboniferous; workable deposits are found in the Coal-measures in nearly all our coalfields and even in the Millstone Grit in Lancashire, Cheshire, the Forest of Dean, the Central Valley of Scotland and in Ayrshire. Besides these more normal occurrences good qualities of refractory clays are found at the following horizons elsewhere.[1]

Pocket deposits of uncertain age (post-Triassic).

Tertiary { Oligocene—basin deposits in Devonshire.
Eocene—Woolwich and Reading beds in Surrey.

Cretaceous—Fairlight Clays (Wealden) Sussex.

Jurassic—Great Oolite and Upper Estuarine Clays, Rutland and Lincolnshire.

Further many inferior grades of kaolinized granite in the china-clay districts of Devon and Cornwall and the waste products from the dressing of high grade china-clays can be made into good fire-bricks, as at Carloggas and in the Calstock district. At Carloggas a very satisfactory product is made from equal parts of (1) fine sandy residue from the "mica" fraction of the washed clay, (2) mica clay, and (3) sand-waste, fired at 1,320°.[2]

The old Tertiary lake basins of Bovey Tracey and Torrington are filled with a great thickness of sands, clays and lignites (over 600 ft. at Heathfield, near Newton Abbot). There is almost every gradation from pure sand through sandy clays to "fat" tenacious ball clays. From these are made among other products firebricks, glazed bricks, vitreous stoneware bricks and acid-proof bricks, as well as many varieties of stoneware, sanitary pipes, enamelled tiles, etc. Some experimental firebricks made at Torrington were found to withstand a temperature up to 1,800° without perceptible softening.[3]

Basic Refractories. The chief substances included in this category are dolomite and magnesite; of less importance are iron ores, bauxite and zirconia.

Dolomite-rock. This has two principal uses in metallurgy, being employed in its natural state as a flux in the smelting of iron ore in the blast-furnace, and as a refractory for lining basic hearths and converters in steel-making. With the first-named use we are not here concerned.

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[1] *Special Repts. Min. Res. Gt. Brit.*, vol. xiv, 1920.

[2] *Ibid.*, p. 157.

[3] *Ibid.*, pp. 161–162.

In this country dolomite-rock, or magnesian limestone, as it is sometimes called, occurs most extensively in the Permian of Notts, Yorkshire, and Durham. It is also found locally in the Carboniferous limestone, and occurs extensively in the Cambrian Durness limestone of the Highlands. The composition of the rock never corresponds exactly to the theoretical composition of the mineral dolomite, since besides the usual impurities, silica, alumina and iron, there is nearly always an excess of calcium carbonate over the dolomite ratio: this exists in calcite. The following are analyses of typical dolomites from various localities, used as refractories, or analysed with a view to ascertaining their suitability for this purpose.

	Permian Dolomite. Sprotborough, Yorks.	Permian Dolomite. Coxhoe Quarries, Durham.	Carboniferous Dolomite. Breedon Hill, Leicestershire.	Carboniferous Dolomite. Risca, Monmouth.	Cambrian Dolomite. Kyle of Durness, Sutherland.[1]
SiO_2 . .	0·14	0·19	0·01	0·17	0·49
Al_2O_3 .	1·90	1·15	0·69	1·41	0·50
Fe_2O_3 .	0·49	0·12	0·04	0·06	0·29
FeO .	0·17	0·28	0·59	0·51	1·52
CaO .	30·07	34·17	30·13	30·70	21·73
MgO .	20·75	17·64	20·65	19·53	13·61
H_2O . .	0·28	0·40	0·70	0·69	0·79
CO_2 . .	46·02	46·01	46·61	45·74	31·45

When intended for use as a refractory the dolomite-rock is first calcined. It is clear that the decomposition of the mineral dolomite takes place in two stages. On first heating the molecule breaks up as follows:

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2$$

The magnesia thus set free combines with the silica and alumina present to form silicates, aluminosilicates or aluminates, forsterite, pyroxene (with or without alumina) and spinel according to the proportions of silica and alumina present, the excess of free magnesia crystallizing as periclase. On further heating the calcium carbonate also dissociates to lime and carbon dioxide, the result being a dense highly crystalline mass of lime and periclase with a network of silicates. The analogy of the first part of this process to the dedolomitization of magnesian limestones subjected to thermal metamorphism is obvious (see p. 146), the chief difference being that in metamorphism the temperature is never high enough to carry out the second part of the decomposition unless sufficient silica is present to combine with the lime. During the calcination there is a considerable reduction of volume, hence the product is technically known as "shrunk dolomite." Since both lime and magnesia are entirely infusible at temperatures attained in steel furnaces this is a very refractory substance, but chemical reactions naturally occur with the constituents of the furnace charges, especially with the iron and the silica of the slag. Hence a certain number of new minerals are formed in addition to the original lime and periclase: the chief of these usually seems to be $3CaO.SiO_2$, tricalcic silicate, a compound not known in nature as a mineral, together with various magnesium silicates. The superficial layer is always deeply stained by iron from the charge and it is difficult to determine the minerals present where the maximum changes must have occurred, but the facts observed seem to be in conformity with the results attained in the investigations carried out at the Carnegie Institute into the behaviour of the system $CaO–MgO–SiO_2$ under laboratory conditions.[1]

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[1] Insoluble residue 28·96 per cent. A very impure dolomite rock.

Bauxite. This substance which, when free from iron or nearly so, is highly refractory, is sometimes used for adding to fire-bricks to increase their refractoriness. It cannot be made into bricks alone, without some clay as a binding material. It is also occasionally used for making very resistant crucibles: the fusion point of pure bauxite is at about 2,000°. All water is driven off before this temperature is reached and the substance has become identical with alumina (corundum).

The exact nature and composition of natural bauxite is still doubtful: it is usually stated to be $Al_2O_3.2H_2O$, while some samples are described as nearly corresponding to $Al_2O_3.H_2O$ (diaspore). Another still more doubtful mineral, hydrargillite, $Al_2O_3.3H_2O$, has also been described. In all probability the true explanation of the discrepancies is that the percentage of water is a function of temperature and pressure, as is known to be the case with the corresponding iron oxides, and the composition should be written $Al_2O_3.xH_2O$. Bauxite probably originates as a precipitate from a colloidal suspension. The common red varieties, such as the samples from Larne, Co. Antrim, contain too much iron for use as refractories: only the pale or nearly colourless varieties can be used. The principal use of bauxite is as an ore of aluminium, but this need not be discussed here.

Iron Ores. Various iron ores, chiefly hæmatite, magnetite or

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[1] Thomas, Hallimond and Radley, *op. cit.*, pp. 79–107.

"purple ore" (burnt pyrites) are occasionally used as linings for iron furnaces: they are not very refractory, but a part of the iron of the lining is reduced and passes into the charge. Siliceous bricks rich in iron oxide are very resistant to oxidizing flue gases, such as those of ordinary steam-boilers.

Neutral Refractories. In this group are included certain substances of a resistant nature which are very inert from the chemical point of view, being neither acid nor basic in character. The most important of them are chromite and graphite, while zirconia is sometimes used on a small scale.

Chromite possesses a very high melting point; about 1,990°, according to Kanolt,[1] and it is scarcely attacked by silica or silicates. It can either be made into bricks with some binding material or be used for patching and repairing open-hearth furnaces.

Graphite. The use of graphite for crucibles for high-temperature work is well known and hardly needs elaboration. It is also sometimes used as a separating layer between the basic lining of an open-hearth furnace and the acid material below.

Zirconia. This is occasionally used on a small scale for crucibles and linings, since it can stand a very high temperature, and is not attacked by either acids or alkalies. A zirconia crucible at a white heat can be dropped into water without cracking.

Glass Sands. Glass in all its varieties is to be regarded as consisting of a homogeneous mixture of various oxides, of which silica is present in largest proportion. From the physical standpoint it is an isotropic substance, without any crystalline structure, and though very hard, rigid and tenacious, it must be regarded as an under-cooled liquid in a state of unstable equilibrium (see Chapter I, p. 9). The different varieties of glass then consist of a fused and cooled mixture of silica with potash, soda or lime, less commonly magnesia or oxides of lead and zinc: the green colour of common bottle-glass is due to iron. Occasionally a little alumina is added for special purposes, besides various colouring or decolorizing matters. The silica is now always employed in the form of quartz sand, though formerly crushed flint was used (hence the name flint glass). For high-grade glass it is essential that the sand should be of extreme purity, free from iron compounds, which would spoil the colour, and also from anything more than a trace of highly resistant minerals, such as zircon, tourmaline or rutile, which would fail to fuse and produce specks and flaws. For common bottle glass a little impurity is not of much importance. A slight green tinge due to a trace of iron can be counteracted by the addition of a trace of manganese which gives the complementary colour. In old houses it can often be seen that the window-glass has a faint violet tint, showing that the addition of manganese was slightly overdone: if some of the panes are slightly green, the contrast is very notable.

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[1] Kanolt. *Jour. Washington Acad. Sci.*, vol. iii, 1913, p. 318.

Before the war nearly all the high-grade glass in this country was made from foreign sands brought over as ballast, chiefly from France (Fontainebleau), Germany (Lippe), and Belgium. Good quality sands are, however, obtainable in this country, as for example from Leighton Buzzard and Kings Lynn (Lower Greensand), Huttons Ambo, near Malton, Yorks (Middle Jurassic) and other places. Besides a high degree of purity, evenness of grain is also an important character, to ensure uniform melting. For the investigation of this property, an elaborate technique and method of expressing results by means of formulæ and curves has been devised.[1]

The mechanical methods of separation of sands into various grade-sizes have now been brought to a high degree of perfection and are widely applicable to the study of sediments of all kinds, and of soils. The methods used naturally vary according to the precise end in view. For technical details reference should be made to the work cited in the footnote.

Abrasives. A section dealing with refractory substances in the strict sense of the word is naturally followed by a few words on a class of substances utilized commercially on account of their value in grinding, scrubbing, and polishing. Here as would naturally be expected hardness is the chief property sought for, resistance to heat and chemical constitution being of minor importance. It is unnecessary to mention here all the innumerable uses to which abrasives are applied: a few only will be named incidentally in cases of some geological interest. For a great number of purposes, industrial and even domestic, quartz sand is largely employed. Quartz is a hard mineral (No. 7 on Mohs' scale) and also tends to occur in sharply angular forms, unless much water-worn. For an abrasive it need not be particularly pure and a proportion of the so-called "heavy minerals" is not harmful: rather the contrary, since most of them are as hard as or harder than quartz. For domestic purposes there are on the market many brands of scrubbing soaps, consisting of a mixture of soap and sand. Certain soft sandstones are largely used in many parts of the country for whitening or reddening stone floors and doorsteps. For this purpose the sandstones must have a soft cement and not too much of it.

Another use of sand, not exactly however as an abrasive, is for the prevention of slipping of steel-tyred wheels on steel rails. All locomotives carry a sand box with a valve for the release of sand if the driving wheels are inclined to skid at starting. Such sand should be sharply angular and free from clayey or chalky material, to give an effective grip. The application of sand on the top layer of tarred roads is of essentially the same nature.

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[1] See especially Boswell, *British Resources of Sands and Rocks used in Glass Making*, 2nd edit., London, 1918, and numerous papers by the same author in various technical journals.

When mention is made of abrasives, the first example that occurs to most people is *emery*. The emery of commerce is essentially a mixture of crystalline alumina with iron oxides (chiefly magnetite and hæmatite), quartz and other minerals. It is found mainly in ancient schistose rocks, in the form of beds, lenses and dyke-like masses of uncertain origin in the Greek islands of Naxos and Nikaria and in Asia Minor. There is now a considerable industry in the mining of crystalline corundum for similar purposes in Ontario (Hastings, Renfrew and Haliburton Counties); in some of the Eastern United States from Alabama to Maine; and in the Transvaal. It is perhaps hardly necessary to remark here that rubies and sapphires are specially pure and clear varieties of corundum.

In recent times emery and corundum have been to a large extent replaced by the artificial substance carborundum, made by fusing together sand and coke in an electric furnace at a very high temperature. Carborundum is now generally used for grinding and polishing rock-sections for the petrological microscope, the first cuts being usually made with a diamond wheel.

For polishing metals and glass a great variety of substances are used: mention may be made of finely divided precipitated ferric oxide, alumina and putty powder.

CHAPTER XII

COLLOIDS IN GEOLOGY

Nature of Colloids. One of the most noteworthy features of the recent advances in physical chemistry is the importance assumed by the study of colloids. This extends not only to the theories of chemistry, but also to the practical side, and many applications of colloids are now of first-class industrial importance. It is a question open to discussion whether or not the application of the theory of colloids has been overdone in certain directions, but at any rate it is clear that this intensive study has thrown much light on many hitherto obscure phenomena, and is likely in future to advance still further our knowledge of many natural processes affecting the mineral constituents of the earth's crust.

Until comparatively recently the study of colloids has not been in a satisfactory state, largely owing to the vagueness of some of the terms employed and their use by different writers in different senses. However it may now be said that a more or less general agreement as to nomenclature has been reached. The most important recent generalization is this, that colloids are not a particular class of substances, but matter of almost any kind in a particular state. We should therefore in strictness speak of substances as being in the colloidal state, rather than as being colloids. For example, to anticipate a little, we may say that it is perfectly clear that in many cases one of the constituents of a colloid may be a crystalline substance, or at any rate a substance capable of crystallizing, such as a metal or a sulphide of a metal.

The term colloid is derived from *colla*, glue. The substances originally included in this class by Graham, the inventor of the term, were then supposed to be homogeneous bodies, incapable of crystallization or of diffusion through membranes. It is now known, however, that Graham's colloids are in point of fact systems of two phases one of which is disseminated in the other in a very finely divided condition, but not in true molecular solution.

According to modern ideas then a colloid is a system of two components in two phases, one component as a rule being greatly in excess. This is spoken of as the continuous phase, the other as the disperse phase. The last-named may be either solid or liquid. It is impossible, however, to draw any hard and fast line of demarcation between suspensions and colloids, or between colloids and true molecular solutions, since they all grade into one another, the special properties of each class depending in the first place on the state of division of the dispersed particles. In the true suspensions and emulsions the suspended particles are comparatively large and visible under the microscope or even macroscopically, and if left undisturbed they settle down quickly by gravity alone. In the true solutions the disperse phase exists as single molecules or small molecular groups, or as dissociated ions, which may be single atoms. At any rate the system appears to be perfectly homogeneous so far as any physical tests can show. Colloidal solutions are intermediate in their properties. The particles are invisible by ordinary microscopic methods, but they can be made visible by special means, and they possess certain peculiar physical properties to be described later. As will be shown shortly the diameter of these particles is usually of the order of 1/100,000 of a millimetre. It is possible that certain highly complex organic molecules may be as large as this, but those of mineral substances are certainly very much smaller.

The following scheme drawn up by Wolfgang Ostwald shows the mutual relations of the different types of dispersed systems here considered.

Dispersoids

Coarse dispersions (suspensions and emulsions)
colloidal dispersions (suspensoids and emulsoids)
molecular dispersions (true solutions)

The meaning of the terms here employed is fairly obvious. In the first group, the coarse dispersions, a distinction is drawn between the cases where the disperse phase is solid or liquid. The term suspension explains itself; in an emulsion the dispersed phase consists of small drops of another liquid, which obviously must not be soluble in the continuous phase: e.g. oil and water. Coarse dispersions are of great geological importance, as, for example, muddy water, from which fine silts are deposited on standing, but this subject need not be discussed here. The extension of the ideas of suspension and emulsion to the colloid group, as governing the distinction between the solid and liquid condition of the disperse phase, is also clear. Most geological colloids appear to be suspensoids, but as will appear later it is believed that silica gels are emulsoids. Another limitation of the geological and mineralogical aspect of the subject arises from the fact that the only types of colloidal systems which need be considered are those in which the continuous phase is water, and the general behaviour of the class of substances represented by glue and gelatine does not concern us.

To sum up very briefly the properties of true colloidal solutions, the viscosity as a rule is very little higher than that of the pure liquid, at any rate in the case of suspensoids (emulsoids are usually more viscous): they are often quite clear and transparent, sometimes coloured and slightly opalescent (pseudo-fluorescence): they possess little or no measurable osmotic pressure and they do not diffuse through semi-permeable membranes. The particles carry electric charges, which are all of the same kind, either positive or negative, and therefore repel one another, but the addition of a small quantity of an electrolyte neutralizes these charges; the particles then tend to adhere to larger aggregates, and the disperse phase either coagulates and settles by gravity as in an ordinary dispersion,[1] or the whole mass solidifies to a jelly-like or horny mass called a gel. Silica appears to be the only substance of geological importance that forms a true gel. Another property of colloids in general is that known as adsorption: this is apparently of great importance in connection with clays, for example, in the study of soils, and will be discussed later. One consequence of this property that may be mentioned here is that colloidal systems are not amenable to treatment by the phase-rule, since the composition of the disperse phase can vary indefinitely.

The conception of the size of the suspended particles may also be expressed in another way, which brings in a reference to the ratio of surface to volume, or what may be considered as the degree of dispersion of the system. Thus a solid cube with an edge of 1 centimetre has a surface of 6 cm^2. or 600 mm^2. If this same cube is now divided so that it is composed of smaller cubes each with an edge of 0·1 cm. or 1 mm., there will then be 1,000 small cubes each with a surface of 6 mm^2., or in all 6,000 mm^2., ten times as much as before, and so on indefinitely. This figure is called the specific surface and is obviously inversely proportional to the diameter of the particles, all being supposed similar in form. Thus if the degree of subdivision is called 10^{-n}, the specific surface is $10^{\div n}$. Now it is found that the properties characteristic of colloids begin to appear when the specific surface is about 10^5, or the diameter of the particles about 10^{-5} cm., and as a general definition it may be stated that in colloids the diameter of the particles of the disperse phase, whether solid or liquid, lies between 10^{-5} and 10^{-7} cm. Such diameters are usually measured by the unit $\mu\mu$, which is one-millionth of a millimetre. Even the higher of these figures is below the limit of ordinary microscopic visibility, but the existence of particles down to about 5 $\mu\mu$ can be demonstrated optically by special means (the so-called "ultra-microscopy"). Particles in colloidal dispersion show the so-called Brownian movements in the ultra-microscope, and it is demonstrable that they carry electrical charges. This subject need not be discussed in detail, but one of the characteristics of such dispersions, depending directly on this special electrical condition, is of great geological importance, namely, the fact that on the addition of a small quantity of an electrolyte, the solid matter hitherto in suspension, the disperse phase, is coagulated or flocculated and settles down as a precipitate. Since all natural waters contain dissolved salts, which are electrolytes, this means in practice that colloidal suspensions cannot be stable in nature, but must give rise to the formation of solid deposits, which may be either crystalline minerals or amorphous substances. Further, substances originally deposited in an amorphous form may become crystalline later, and in fact usually do so. It certainly seems to be a fact that "solid" precipitates of all kinds formed from colloidal suspensions are in general unstable, and this is only natural if we consider that the concentration of the phases can vary indefinitely and they therefore can never be in a true state of equilibrium. Obviously the properties must depend mainly on the nature and amount of the electrical charges on the particles, and the degree of ionization in the solutions.

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[1] In such comparatively coarse disperse systems as muddy water settling of the mud is hastened by the presence of electrolytes.

Colloidal Silica. When the term colloid is mentioned in connection with minerals, the first example that naturally occurs to every one is hydrated silica. This was one of the substances first described by Graham 60 years ago as an example of his colloids, thereby meaning chiefly substances incapable of diffusing through a semipermeable membrane. It also shows exceedingly well the formation of a gel and can be obtained in a "solid" state with a remarkably small proportion of silica as compared with the amount of water.[1] However it has now to be recognized that from the mineralogical point of view a silica gel is exceptional, in that it is in all probability an emulsoid and not a suspensoid, like most other colloidal systems of geological and mineralogical significance.

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[1] The word *solid* is here used in a more or less popular sense.

It is clear then that hydrated silica, or to put it more precisely, systems of silica and water, can exist in a colloidal form ; but the study of these systems is greatly complicated by the existence, at any rate in compounds (silicates), of silicic acid radicles of definite composition, such as metasilicic acid, orthosilicic acid and others. This is shown by the constancy of composition and properties of many of the commonest rock-forming minerals. Thus among the metasilicates we have the pyroxenes and amphiboles ; among the orthosilicates, the olivine group, nepheline, anorthite, and the micas, all belonging to the primary magmatic stages of crystallization. Then again there are the very well-characterized silicates of aluminium : andalusite, kyanite and sillimanite and the garnet group, the last-named being also orthosilicates, among minerals of the metamorphic series. Orthoclase, microcline and albite are perfectly definite salts of a more complex silicic acid and the zeolites show a great variety of ratios between acid and base, these ratios being, however, always whole numbers. Hence it is clear that silica and water form definite acids, though whether these can be isolated as such is doubtful. Many writers, in their discussions of the rôle of silica in mineral formation have apparently suffered from some confusion of ideas on this point, as it by no means follows that a hydrated silica gel in the colloidal state can combine directly with bases to form silicates. The subject of the present section, however, is the properties and behaviour of hydrogels composed of silica and water.

Colloidal silica can be prepared by treating a solution of sodium silicate (water glass) with hydrochloric acid and removing the sodium chloride formed by dialysis. The liquid then left in the semi-permeable vessel is a gel, which on concentration by evaporation passes spontaneously into a jelly-like mass and then into a hard amorphous substance. It belongs to the class of *irreversible* colloids and cannot again be brought into a liquid form by addition of water or by warming, like gelatine or glue. Colloidal silica of this kind, when hard, is however distinctly more soluble than any form of crystalline silica, and dissolves fairly easily in caustic potash. It is quite clear that the silica of certain silicates can be converted into a colloidal form : on this fact depends the ordinary petrographic staining-test for nepheline : the section supposed to contain it is treated first with a mineral acid, which decomposes the nepheline and leaves a mass of silica jelly which is then treated with an aniline dye : the colouring matter of the dye is adsorbed and the nepheline crystals are stained. This adsorption proves that the silica exists in the colloidal state, as a gel. The felspars, however, are not affected in this way. It is probable also that the silica set free during the hydrolysis of alkali silicates, as in the formation of kaolin from orthoclase, is released in the colloidal form. Silica produced by processes of this class is undoubtedly the source of the deposits of secondary silica which are so common nearly everywhere and to which so many unnecessary names are applied. Of this class of minerals opal is perhaps the most characteristic and the best defined. Analyses of opal always show the presence of water up to 10 per cent., and true opal always seems to be isotropic. Here also must in all probability be assigned the numerous varieties of minerals conveniently classed as chalcedony. These minerals are doubly refracting and therefore in their present condition differ from opal. A detailed study of the optical properties shows that they do not consist of quartz, true chalcedony being optically negative. It therefore seems probable that chalcedony was originally deposited in the colloidal state, but at a later stage has crystallized, the process probably being accompanied by loss of water.

A great number of names have been applied to silica minerals of this kind, such as chalcedony, jasper, onyx, prase, chrysoprase, agate and so forth, according to variations of colour and structure. They are frequently nodular or botryoidal in structure and often show banding. Such minerals are very commonly found in fissures in rocks and in cavities of various kinds, especially steam bubbles in lavas, which are often on a large scale. Banded agates and similar types occurring in this way are very significant as to the originally colloidal nature of the silica, and a specially important piece of evidence is found in the fact that they often show a strong adsorptive power for colouring matters. Large specimens of this kind, often called geodes, are sometimes found to be hollow, and occasionally contain water. This is obviously water separated from the original silica gel, the silica itself being deposited as cryptocrystalline chalcedony. This separation is doubtless brought about in the usual way by the penetration of a salt solution containing free ions into the geode.

In a few instances, though but rarely, colloidal silica in a soft jelly-like form has been found in a natural state ; a classical and much-quoted example occurred during the making of the Simplon Tunnel, where as is well known the engineers were much hampered by encountering great volumes of hot water : the two phenomena were obviously connected.

Colloform Structures. There is no doubt that a very large number of naturally occurring substances, both minerals and rocks, have been deposited from a state of colloidal dispersion. It must be specially noted, however, that this statement does not imply that these substances are now in the colloidal state : as a matter of fact many of them, perhaps the majority, are actually crystalline, but they possess structures which give the clue to their true manner of origin. Such structures are conveniently summed up in the general category of *colloform*. This category cannot be precisely defined, but it includes all those numerous varieties of form generally described as botryoidal, reniform, mammillated, nodular and forth, of which good examples are afforded by many forms of silica, the oxides of manganese, and limonite. Here also must be included the many varieties of stalactite and stalagmitic growths, oolites and pisolites and so forth ; in fact most forms which can be conveniently summed up as concretionary. It is specially to be noted that very many of these show distinctly both radial and concentric structures, often made particularly clear by colour variations or other forms of banding. The differences of colour are often due to adsorption, or in other cases to rhythmical precipitation during diffusion, as worked out in detail by Leisegang.[1]

Colloform Iron-oxide and Manganese Minerals. The ferric oxide minerals, both hæmatite and the various hydrated forms, very commonly show structures strongly suggestive of an origin from colloidal dispersions. Hæmatite can and often does form very perfect tabular or prismatic crystals, with brilliant metallic lustre, but it is probably even commoner in various types of botryoidal, reniform or mammillated structures, showing very well-marked concentric and radial arrangements. Such are exceedingly well seen in the " Kidney ore " of Cumberland and Furness, which is formed by bodily replacement of Carboniferous limestone, a process of metasomatism. Similar structures are also to be seen in veins in the Skiddaw Slates underlying the limestone, or formerly covered by the limestone : these can hardly be regarded as replacements, but rather as normal vein-fillings. Concretionary hæmatite is common in very many other localities in deposits belonging to both these types.

The substance commonly called limonite is now known to be a hydrated ferric oxide with a variable proportion of water, and not a definite hydrate. It never forms simple crystals, but always shows a radial, concretionary and banded structure, very like that of hæmatite, but distinguished by its brown colour and streak. Again, göthite, $Fe_2O_3.H_2O$, the only ferric hydrate possessing a constant composition, often forms radial and concentric masses of fibrous prismatic crystals, strongly suggestive of a colloidal origin.

This type of structure is also highly characteristic of several of the numerous oxides and hydroxides of manganese, especially psilomelane and pyrolusite, while manganese oxides are very widely distributed as the so-called dendrites, branching aggregates in two or three dimensions with a very strong resemblance to fossilized plants. They are most commonly developed in two dimensions only, along joints, bedding or cleavage planes, and are believed to be due to colloidal precipitation.

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[1] Liesegang, *Geologische Diffusionen*. Dresden, 1913.

Colloform Carbonates. The types of structure observed in many varieties of carbonate rocks and minerals also belong to this category. It is only necessary here to mention a few very briefly, such as the ooliths and pisoliths so common in limestones (and in many iron ores) ; the remarkable concretions of calcite so well seen in the Magnesian Limestone of Durham ; many occurrences of aragonite, and the common forms of zinc carbonate, in the oxidized portions of blende deposits (e.g. Derbyshire and Vieille Montagne or Altenberg in Belgium).

Many of the deposits comprised under the general designation of stalactites, stalagmites, calc-sinter, travertine and so on show very clearly structures of the colloform type, and it is a fair inference that the calcium carbonate thus deposited has passed through a colloidal stage, although now clearly crystalline.

The well-known variety of fluorspar known in Derbyshire as " Blue John " is another very good example in a different mineral group, while Schalenblende, a banded variety of zinc sulphide ore, and wood tin, tin dioxide formed by oxidation of stannite in Cornwall and Bolivia, are other good instances among minerals of economic interest.

It is perhaps somewhat too early to draw up any generalities on this subject. There can be no doubt however that deposition from colloidal suspensions has played a very important part in formation of minerals from aqueous solutions, especially in the upper and cooler zones of the earth's crust, where there is free circulation of aqueous solutions, usually very dilute, and commonly associated with abundant electrolytes. How the mineral substances originally get into the colloidal condition is, however, by no means clear.[1]

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[1] For an admirable summary of the present state of knowledge of the part played by colloids in geology, with an extremely complete bibliography, see Scott, *The Application of Colloid Chemistry to Mineralogy and Petrology*, 4th Report on Colloid Chemistry and its General and Industrial Applications (*Brit. Assoc. Adv. Sci.*), 1922, pp. 204–243.

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